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THE STRUCTURE OF DI-*tert*-BUTYLNAPHTHALENESULPHONIC ACIDS[1]

MARCEL MENARD, LEONARD MITCHELL, JACQUELINE KOMLOSSY, AVERIL WRIGLEY, AND FRANCIS L. CHUBB

ABSTRACT

Commercial sodium di-*tert*-butylnaphthalenesulphonate has been resolved into its isomers, which were shown to be sodium 2,6- and 2,7-di-*tert*-butylnaphthalene-4-sulphonates.

Sodium di-*tert*-butylnaphthalenesulphonate is known as an effective central inhibitor of the cough reflex (1). Although some authors (1) refer to this antitussive drug as sodium 2,6-di-*tert*-butylnaphthalenesulphonate, its mode of preparation suggests that it is a mixture of at least two different isomers. It is prepared (2) by a Friedel–Crafts alkylation of naphthalene with 2 moles of *tert*-butyl chloride followed by sulphonation of the butylation product. Since several workers (3) have shown that *tert*-butylation of naphthalene gives a mixture containing about equal parts of 2,6- and 2,7-di-*tert*-butylnaphthalene, the commercial product can be inferred to consist of approximately equal quantities of the corresponding sulphonates. The purpose of this work was to isolate the isomers of sodium di-*tert*-butylnaphthalenesulphonate and to determine their structure.

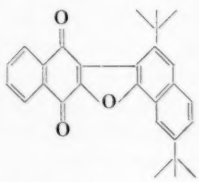
Reaction of commercial sodium di-*tert*-butylnaphthalenesulphonate with thionyl chloride according to a procedure recently developed by Bosshard *et al.* (4) gave a mixture from which two isomeric sulphonyl chlorides could be isolated by fractional crystallization: one melting at 167–169°, insoluble in cold ligroin; the second melting at 117–118°, moderately soluble in ligroin. Hydrolysis of these sulphonyl chlorides with sodium hydroxide regenerated the pure sulphonates. The sulphonate obtained from the higher-melting isomer was shown to be sodium 2,7-di-*tert*-butylnaphthalenesulphonate by conversion to 2,7-di-*tert*-butylnaphthalene (3) with 60% sulphuric acid. In the same way the sulphonate obtained from the lower-melting sulphonyl chloride was related to 2,6-di-*tert*-butylnaphthalene.

In order to determine the position of the sulphonic acid group of these compounds, sulphonation of 2,6- and 2,7-di-*tert*-butylnaphthalene under conditions which usually bring about α-sulphonation of naphthalene and naphthalene derivatives (5) was carried out. Reaction of these sulphonic acids with thionyl chloride gave the same sulphonyl chlorides as those isolated from the commercial product. On the other hand alkaline fusion of the sulphonates yielded naphthols which readily coupled with phenyldiazonium chloride to give orange-red azo dyes; these were easily reduced by stannous chloride to aminonaphthols, which in turn gave yellow quinones on oxidation. The quinone obtained from the 2,6-di-*tert*-butylnaphthol was found to be identical with the quinone obtained by Fieser and Price (6) from a chromic acid oxidation of 2,6-di-*tert*-butylnaphthalene.

[1]*Manuscript received December 8, 1960.*
Contribution from the Research Laboratories, Frank W. Horner Limited, Montreal, Quebec.

This quinone was later shown by Crawford and Glesmann (3) to be 2,6-di-*tert*-butyl-1,4-naphthoquinone. Chromic acid oxidation of 2,7-di-*tert*-butylnaphthalene under similar conditions also gave a quinone, identical with that resulting from the coupling reaction of the 2,7-di-*tert*-butylnaphthol, reduction of the azo dye, and oxidation of the aminonaphthol. Furthermore, we found that the disubstitution product obtained by Buu-Hoi and Demerseman (7) from the alkylation of α-naphthol with *tert*-butyl bromide, which they suggest may be a 4,*x*-di-*tert*-butyl-1-naphthol, was identical with the naphthol obtained from the alkaline fusion of 2,6-di-*tert*-butylnaphthalenesulphonate. Thus the sulphonic acid group of the starting sulphonates can only be in the 1 or 4 positions.

Of the two possible α-positions, position 4 seemed more probable: sulphonation of 2,6- and 2,7-dimethylnaphthalene occurs preferentially in position 4 (8) and furthermore position 1 is subjected to the steric effect of the tertiary butyl group. Position 1 was finally eliminated by the fact that yellow di-*tert*-butyldinaphthofuranquinones, I and II, giving an intense blue color with sulphuric acid, could be isolated from the reaction of 2,6- and 2,7-di-*tert*-butylnaphthols with 2,3-dichloro-1,4-naphthoquinone. This cyclization reaction was shown by Buu-Hoi and Demerseman (7) to be characteristic of naphthols having an unsubstituted position adjacent to the OH group, which holds only if the hydroxyl group of the 2,6- and 2,7-di-*tert*-butylnaphthol occupies position 4. Consequently the sulphonic acid group in the starting sulphonates must occupy position 4.



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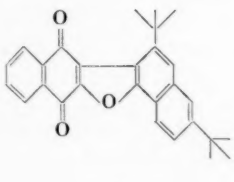
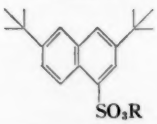


II

Reaction of 2,7-di-*tert*-butylnaphthalene-4-sulphonyl chloride with alcohols in pyridine solution afforded a series of esters which are reported in Table I. The methyl and ethyl ester of 2,6-di-*tert*-butylnaphthalene-4-sulphonic acid were prepared by reaction of the acid with diazomethane and diazoethane in ether solution.

TABLE I



R	M.p. (solvent)	Analysis			
		% C, calc.	% H, calc.	% C, found	% H, found
Ethyl	138–139° (EtOH)	68.93	8.10	69.32	8.20
n-Propyl	109–110° (EtOH)	69.57	8.35	69.57	8.36
n-Butyl	74–75° (EtOH)	70.17	8.57	70.54	8.49
n-Hexyl	77–78° (EtOH)	71.24	8.97	71.28	8.99
Cyclohexyl	124° (EtOH)	71.60	8.51	71.77	8.48
Phenyl	78–79° (EtOH)	72.69	7.12	72.86	7.12
Glycolyl	85–87° (CCl_4 – pet. ether)	65.90	7.74	66.93	8.31
Glyceryl	135–136° (CCl_4 – pet. ether)	63.93	7.67	64.47	7.72

EXPERIMENTAL

2,6- and 2,7-Di-tert-butylnaphthalene-4-sulphonyl Chloride

The commercial mixture of sodium di-*tert*-butylnaphthalenesulphonate (34.6 g, 0.1 mole), thionyl chloride (25 ml), and dimethylformamide (0.8 ml) were heated for 1 hour on the steam bath. The excess of thionyl chloride was evaporated under reduced pressure and the residue was triturated with 100 ml of cold water, filtered, and dried over sulphuric acid. The dried mixture of sulphonyl chlorides (36.2 g) was recrystallized in 100 ml of ligroin, with the aid of 3 g of decolorizing charcoal; there was so obtained 12.3 g (36%) of 2,7-di-*tert*-butylnaphthalene-4-sulphonyl chloride, m.p. 163–165°. The analytical sample, recrystallized from ligroin, had a melting point of 167–169°. Calc. for $C_{18}H_{23}O_2SCl$: C, 63.79; H, 6.84%. Found: C, 63.97; H, 7.01%.

Concentration of the mother liquors and repeated recrystallization of the residue from isopropanol gave 8.2 g (24.3%) of 2,6-di-*tert*-butylnaphthalene-4-sulphonyl chloride, m.p. 117–118°. Calc. for $C_{18}H_{23}O_2SCl$: C, 63.79; H, 6.84%. Found: C, 64.03; H, 6.97%.

Sodium 2,7-Di-tert-butylnaphthalene-4-sulphonate

To a boiling solution of 5 g of 2,7-di-*tert*-butylnaphthalene-4-sulphonyl chloride in 20 ml of ethanol there was slowly added a solution of 1.2 g of sodium hydroxide in 40 ml of water. The mixture was refluxed for 4 hours, the solvents removed, and the residue recrystallized from water to give 4.8 g (85%) of colorless waxy plates. Calc. for $C_{18}H_{23}O_3SNa.2H_2O$: C, 57.15; H, 7.20; S, 8.47%. Found: C, 57.44; H, 7.12; S, 7.49%.

Sodium 2,6-Di-tert-butylnaphthalene-4-sulphonate

Hydrolysis of 2,6-di-*tert*-butylnaphthalene-4-sulphonyl chloride with sodium hydroxide gave 90% of colorless needles from nitromethane, m.p. >360°. Calc. for $C_{18}H_{23}O_3SNa.2H_2O$: C, 57.15; H, 7.20; S, 8.47%. Found: C, 57.51; H, 7.09; S, 8.08%.

2,7-Di-tert-butylnaphthalene

A mixture of 8 g of sodium 2,7-di-*tert*-butylnaphthalene-4-sulphonate and 100 ml of a 60% solution of sulphuric acid was stirred and heated at 150–160° for 5 hours, cooled, poured into 1 liter of cold water, and extracted with ether. The ether extracts were washed with water, dried, and concentrated. After recrystallization from ethanol the residue yielded 2.8 g of colorless needles, m.p. 103–104°; these gave no depression of melting point when mixed with a sample prepared according to Price *et al.* (3).

2,6-Di-tert-butylnaphthalene

Hydrolysis of 5 g of sodium 2,6-di-*tert*-butylnaphthalene-4-sulphonate in 60% sulphuric acid gave 1.7 g of flat needles, m.p. 145–146°. Identity of this material with pure 2,6-di-*tert*-butylnaphthalene (3) was confirmed by a mixed melting point.

2,6-Di-tert-butylnaphthalene-4-sulphonic Acid

Chlorosulphonic acid (56 g, 0.48 mole) was slowly added, with stirring and cooling, to a solution of 116 g (0.48 mole) of pure 2,6-di-*tert*-butylnaphthalene in 240 ml of dichloroethane. The reaction mixture was allowed to stand for 2 hours at 0–5° and the solvent was removed at room temperature under reduced pressure. The residue, a heavy oil, started to crystallize upon the addition of 0.5 mole of water; recrystallization from dichloroethane gave 155 g (95%) of the hydrate of 2,6-di-*tert*-butylnaphthalene-4-sulphonic acid as colorless plates, m.p. 158°. Calc. for $C_{18}H_{24}O_3S.H_2O$: C, 63.87; H, 7.74%; M.W., 338.5. Found: C, 63.45; H, 7.76%; N.E., 339.3.

2,7-Di-tert-butylnaphthalene-4-sulphonic Acid

2,7-Di-*tert*-butylnaphthalene (3.3 g) dissolved in 7 ml of dichloroethane and treated, as described for the 2,6-isomer, with 1.8 g of chlorosulphonic acid gave 2.6 g (55%) of the hydrate of 2,7-di-*tert*-butylnaphthalene-4-sulphonic acid, m.p. 140–142° (chloroform – petroleum ether). Calc. for $C_{18}H_{24}O_3S.H_2O$: C, 63.87; H, 7.74%; M.W., 338.5. Found: C, 62.54; H, 7.82%; N.E., 339.4.

2,6-Di-tert-butylnaphthalene-4-sulphonyl Chloride

The anhydrous residue obtained from the reaction of 56 g of chlorosulphonic acid and 116 g of 2,6-di-*tert*-butylnaphthalene as described above was mixed, in a distillation apparatus, with 91 ml of thionyl chloride and 3 ml of dimethylformamide. The mixture was stirred and heated on the steam bath until it became homogeneous (½ hour). During that time most of the excess of thionyl chloride had distilled over; the remainder was removed under reduced pressure. The residue was triturated with cold water and extracted with ether. The combined ether extracts were dried and concentrated; the solid residue, recrystallized from alcohol, gave 133.5 g (86%) of colorless prisms, m.p. 117–118°. These gave no depression of melting point when mixed with a sample of the sulphonyl chloride obtained from the commercial mixture of sulphonates.

The amide was prepared by passing dry ammonia through a solution of the chloride in tetrahydrofuran, removing the solvent, triturating the residue with water, and recrystallizing the dried solid from ligroin: m.p. 160–161°. Calc. for $C_{18}H_{25}O_2NS$: C, 67.67; H, 7.89; N, 4.38%. Found: C, 67.70; H, 7.89; N, 4.37%.

2,7-Di-tert-butylnaphthalene-4-sulphonyl Chloride

The anhydrous 2,7-di-*tert*-butylnaphthalene-4-sulphonic acid, treated as described above with thionyl chloride and dimethylformamide, gave 90% of colorless prisms, m.p. 167–169°; this melting point was not depressed by mixing with the 2,7-di-*tert*-butylnaphthalene-4-sulphonylchloride obtained from the commercial mixture of sulphonates.

The amide was prepared as above, m.p. 165°. Calc. for $C_{18}H_{25}O_2NS$: C, 67.67; H, 7.89; N, 4.38%. Found: C, 67.17; H, 8.06; N, 4.59%.

2,7-Di-tert-butyl-4-naphthol

Potassium 2,7-di-*tert*-butylnaphthalene-4-sulphonate (30 g), 100 g of potassium hydroxide, and 30 ml of water were heated slowly in an iron crucible until the mixture melted and the potassium salt of the naphthol floated on the surface of the melt as a dark-brown oil. The mixture was cooled, dissolved in water, acidified with hydrochloric acid, and extracted three times with ether. The combined ether extracts were washed with water, dried, and concentrated. The residue, a heavy black oil, was distilled under reduced pressure and yielded 14.2 g of a yellow oil, b.p. 170–180°/4 mm. Crystallization of this oil in ligroin afforded 8 g (41%) of colorless needles, m.p. 125–126°. The analytical sample, recrystallized from ligroin, had a melting point of 127–128°. Calc. for $C_{18}H_{24}O$: C, 84.32; H, 9.44%. Found: C, 84.47; H, 9.43%.

2,6-Di-tert-butyl-4-naphthol

Alkaline fusion of potassium 2,6-di-*tert*-butylnaphthalene-4-sulphonate carried out as described above for the 2,7-isomer, gave 63% of a reddish oil, b.p. 190°/3 mm, which afforded 25% of colorless crystals, m.p. 142°. The identity of this compound with the one obtained by Buu-Hoi and Demerseman (7) from *tert*-butylation of α-naphthol was confirmed by a mixed melting point.

2,7-Di-tert-butyl-1-phenylazo-4-naphthol

Aniline (3.4 g), dissolved in 11 ml of concentrated hydrochloric acid and 11 ml of water,

was diazotized with a solution of 2.8 g of sodium nitrite in 14 ml of water. The resultant solution of phenyldiazonium chloride was added dropwise to a well-stirred mixture of 8 g of 2,7-di-*tert*-butyl-4-naphthol, 30 ml of 10% sodium hydroxide solution, and 20 ml of tetrahydrofuran cooled to 5°. The mixture was then stirred for 30 minutes at 5° and allowed to stand overnight. Most of the tetrahydrofuran was removed under reduced pressure and the water was decanted from the heavy dark oil, which was then boiled with 40 ml of glacial acetic acid and filtered hot. After cooling and filtering, the crude precipitate was recrystallized from 200 ml of acetic acid to yield 2.6 g (28%) of red crystals, m.p. 229–239°. Calc. for $C_{24}H_{28}ON_2$: C, 79.96; H, 7.83; N, 7.77%. Found: C, 79.91; H, 7.88%; N, 7.74%.

2,6-Di-tert-butyl-phenylazo-4-naphthol

The coupling reaction of 4 g of 2,6-di-*tert*-butyl-4-naphthol with phenyldiazonium chloride was carried out as described above for the 2,7-isomer. After removal of the tetrahydrofuran, a solid was obtained which was filtered and recrystallized from acetic acid to give 2.2 g of the orange-red azo compound, m.p. 204–206°. Calc. for $C_{24}H_{28}ON_2$: C, 79.96; H, 7.83; N, 7.77%. Found: C, 79.80%; H, 7.80%; N, 7.42%.

2,7-Di-tert-butyl-1,4-naphthoquinone

(a) From 2,7-Di-tert-butylnaphthalene

A solution of 2.6 g of chromium trioxide in 4.4 ml of acetic acid and 2.9 ml of water was added dropwise to a stirred slurry of 2.0 g of 2,7-di-*tert*-butylnaphthalene in 11 ml of acetic acid maintained at 60°. After the addition was complete, the mixture was stirred for ½ hour at 60°, poured into 150 ml of cold water and extracted with ether. The ether extracts were washed with water, dried, and concentrated; the residue crystallized from dilute alcohol and yielded 2.0 g (89%) of yellow needles, m.p. 72°. Calc. for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20%. Found: C, 79.71%; H, 7.92%.

Reaction of the quinone with 2,4-dinitrophenylhydrazine gave a compound which crystallized from acetic acid as orange-red needles, m.p. 250–251°. Calc. for $C_{24}H_{26}O_8N_4$: C, 63.98; H, 5.82; N, 12.44%. Found: C, 63.79; H, 5.90; N, 12.41%.

(b) From 2,7-Di-tert-butyl-1-phenylazo-4-naphthol

A solution of 8 g of stannous chloride in 24 ml of concentrated hydrochloric acid was added to a boiling slurry of 1.9 g of 2,7-di-*tert*-butyl-1-phenylazo-4-naphthol in 80 ml of methanol; the azo compound slowly dissolved and after 1½ hours the solution was colorless. It was concentrated to a volume of approximately 30 ml and cooled. The crystalline 2,7-di-*tert*-butyl-1-amino-4-naphthol hydrochloride was filtered and slurried in a solution of 0.6 ml of sulphuric acid in 12 ml of water. A solution of 0.4 g of potassium dichromate in 6 ml of water was added to the resultant mixture and the whole was heated at steam-bath temperature for 5 minutes, cooled, diluted with water, and extracted with ether. The ether extracts were washed with water, dried, and concentrated. Upon reaction with 2,4-dinitrophenylhydrazine the liquid residue gave an orange-red compound, m.p. 250–251°, found by a mixed melting point determination to be identical with the addition compound obtained as under (*a*).

2,6-Di-tert-butyl-1,4-naphthoquinone

(a) From 2,6-Di-tert-butylnaphthalene

Oxidation of 13.8 g of 2,6-di-*tert*-butylnaphthalene with 18 g of chromium trioxide as described above for the 2,7-isomer yielded a solid compound after the reaction mixture was poured into water. Recrystallization of this solid from ethanol gave 7.4 g (48%) of yellow needles, m.p. 85–86° (lit. (6) m.p. 83.5–84.5°).

(b) From 2,6-Di-tert-butyl-1-phenylazo-4-naphthol

Reduction of this azo compound (0.23 g) with stannous chloride and oxidation of the aminonaphthol with potassium dichromate gave 0.1 g (60%) of yellow needles, m.p. 85–86°, not depressed when mixed with a sample prepared according to (*a*).

Esters of 2,7-Di-tert-butylnaphthalene-4-sulphonic Acid

A solution of 0.15 mole of the appropriate alcohol in 80 ml of anhydrous pyridine was cooled to −10°; 0.08 mole of powdered 2,7-di-*tert*-butylnaphthalene-4-sulphonyl chloride was added at such a rate that the temperature would not exceed −5°; the resultant mixture was stirred for 2 hours at 0–5° and poured into water (500 ml). In those cases where a solid ester was obtained it was separated by filtration and recrystallized from the appropriate solvent; when an oil was obtained, the ester was extracted with ether and isolated by the usual procedure. Physical data for the esters involved are included in Table I.

Esters of 2,6-Di-tert-butylnaphthalene-4-sulphonic Acid

A slight excess of an ethereal solution of the appropriate diazoalkane was added to a cooled solution of the monohydrate of 2,6-di-*tert*-butylnaphthalene-4-sulphonic acid in ether. After standing overnight the solvent was removed and the ester isolated. The methyl ester was obtained as a solid which crystallized from methanol as colorless prisms, m.p. 123–124°. Calc. for $C_{19}H_{26}O_3S$: C, 68.22; H, 7.84; S, 9.58%. Found: C, 68.58; H, 7.95; S, 9.94%.

The ethyl ester was obtained as a colorless oil, b.p. 180–185/1 mm. Calc. for $C_{20}H_{28}O_3S$: C, 68.93; H, 8.10%. Found: C, 68.92%; H, 8.26%.

3′,7′-Di-tert-butyldinaphtho(1′,2′-2,3)(2″,3″-4,5)furan-1″,4″-quinone

A solution of 2.6 g of 2,6-di-*tert*-butyl-4-naphthol and 2.3 g of 2,3-dichloro-1,4-naphthoquinone in 15 ml of anhydrous pyridine was stirred and refluxed for 18 hours. After cooling, the mixture was diluted with methanol and filtered. Recrystallization of the filter cake from toluene gave 0.52 g (13%) of yellow needles, m.p. 354–355°. Calc. for $C_{28}H_{26}O_3$: C, 81.92; H, 6.38%. Found: C, 81.78; H, 6.53%.

3′,6′-Di-tert-butyldinaphtho(1′,2′-2,3)(2″,3″-4,5)furan-1″,4″-quinone

A solution of 4.6 g of 2,3-dichloro-1,4-naphthoquinone and 5.2 g of 2,7-di-*tert*-butyl-4-naphthol in 30 ml of pyridine was stirred and refluxed for 18 hours. After cooling, the mixture was filtered and the filtrate concentrated to a volume of approximately 10 ml. The pyridine solution was then diluted with methanol and allowed to stand overnight. Filtration and recrystallization of the filter cake in toluene–methanol afforded 1.1 g (15%) of orange-yellow needles, m.p. 217–218.° Calc. for $C_{28}H_{26}O_3$: C, 81.92; H, 6.38%. Found: C, 82.21; H, 6.57%.

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THE EQUILIBRIUM DIAGRAMS, HEATS OF MIXING, DIPOLE MOMENTS, DENSITIES, AND BOILING POINTS OF THE SYSTEM ACETONE–CHLOROFORM–BENZENE[1]

A. N. Campbell, E. M. Kartzmark, and H. Friesen

ABSTRACT

The equilibrium diagrams show that a compound, stable in the solid state, is formed in the system chloroform–acetone, but no compound is formed in the binary systems chloroform–benzene and acetone–benzene. The ternary equilibrium diagram, the heats of mixing, and the dipole moments, all show that this compound continues to exist in the presence of benzene, up to a high concentration of benzene. Since a series of ternary mixtures is shown to exist having zero heat of mixing, it was thought that this series of mixtures might behave in a pseudoideal manner, but the determinations of density (molar volume) and boiling point show that this is not so.

The existence of a compound, $CHCl_3$—$(CH_3)_2CO$, in mixtures of chloroform and acetone has been shown to be probable (1): the compound is an obvious example of hydrogen bonding. We thought it would be interesting to investigate the effect of adding the non-polar liquid benzene to the acetone–chloroform system. The systems benzene–chloroform, benzene–acetone, chloroform–acetone, and the ternary system benzene–chloroform–acetone, were investigated in regard to the following properties: freezing point diagrams, heats of mixing, dipole moments, densities, and boiling points.

EXPERIMENTAL

Freezing-Point Diagrams

The technique has often been described. It consisted essentially of a double-jacketed vessel containing a system of known composition. By controlling the degree of vacuum in the jacket, any desired rate of cooling could be obtained. The cooling agent was liquid nitrogen. Temperatures were measured by means of a copper–constantan thermocouple and a recording potentiometer.

Heats of Mixing

Heats of mixing were determined by having a weighed amount of one liquid in a magnetically stirred vacuum-walled calorimeter and the second liquid, also weighed, in a second such vessel. One set of junctions of a 20-junction copper–constantan thermopile was in the calorimeter and the other in the other vessel so that the thermopile measured the difference in temperature of the two vessels; allowance was made for slight original difference in temperature. The thermopile had a sensitivity of about 0.2° C, corresponding to the minimum reading of the recorder chart. A suitable quantity of the second liquid was forced through a course capillary into the calorimeter, the amount being determined by weighing at the end of the experiment.

The average rise in temperature was about 7°. The usual method of radiation correction was applied and the water equivalent of calorimeter and contents was determined electrically for each individual experiment. Current through the immersed platinum heating coil was determined from the voltage drop over a standard resistance. By this method temperatures are not measured as such; the electrical input is multiplied by the ratio of two vertical lines on the recorder graph.

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Contribution from the Chemistry Department of the University of Manitoba, Winnipeg, Manitoba.

The ternary system was treated in the following way. Stock solutions were made up containing fixed mole fractions of benzene, e.g.

$$0.1\ N_{C_6H_6} \qquad 0.9\ N_{CHCl_3}$$

$$0.1\ N_{C_6H_6} \qquad 0.9\ N_{(CH_3)_2\cdot CO}$$

These were mixed in varying proportions and the heat effect measured, corrections being applied for the heat exchange that had occurred in the original mixing of the quantities of stock solution used. This procedure was reported for each 1/10th mole fraction benzene; the results were plotted as in Fig. 5. The presence of benzene lowered the heat effect (evolution) with regard to acetone–chloroform because, on mixing benzene with acetone a small quantity of heat is absorbed, and in the case of benzene–chloroform, although heat is evolved, the quantity is small.

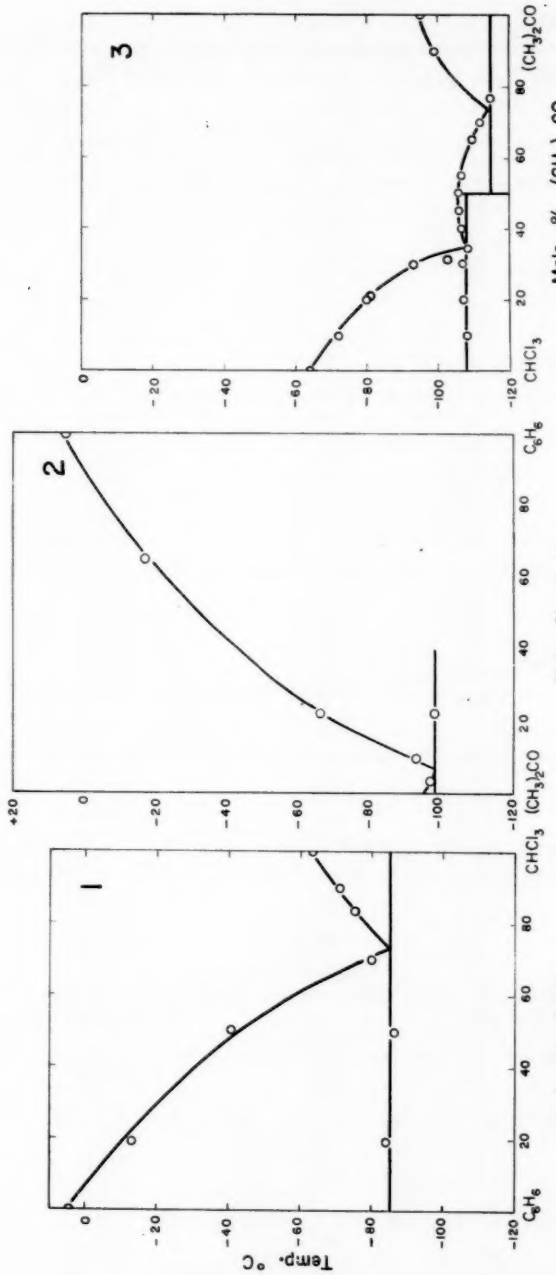
Dipole Moments

Dielectric constants of known mixtures of acetone, chloroform, and benzene were determined on a General Radio capacitance bridge, using an audio-frequency oscillator at 1000 cycles to energize the bridge and amplifying the signal to headphones. The arrangement worked well for low dielectric constants. Thus, it reproduced exactly the dielectric constants of pure benzene and pure chloroform but not the relatively high dielectric constant of acetone. Since, however, we were only interested in ternary solutions containing at least 90 mole% benzene, we experienced no trouble.

We argued in our paper on the energy of hydrogen bonding (2) that, however highly dissociated the compound of acetone and chloroform may be when the components are present in equimolecular proportion, the dissociation must be reduced to zero, when one or other component is present in infinite excess. A similar argument should apply to the dipole moment but here both components should be in the presence of an infinite excess of benzene, if the true molecular polarization is to be deduced. For this purpose we determined the dielectric constants over a range of chloroform–acetone ratios, in benzene as solvent. Two series of measurements were made: (1) in 90 mole% benzene; (2) in 95 mole% benzene. Measurements were not carried to greater dilution because the magnification of the experimental error rendered the final result of little value.

Boiling Points

A very complete investigation of the boiling points of the ternary system has been made by Reinders and de Minjer (3). The system is non-ideal, an azeotropic maximum occurring in the acetone–chloroform system. It seemed to us, however, from our measurements of heat of mixing that a curve of pseudoideal behavior might traverse the ternary diagram. At least, there certainly exists such a series of solutions which are formed with zero heat of mixing. If this series were really ideal, members of it would form from the components without volume change and the partial pressures would agree with Raoult's law. For this purpose, we re-established the apparatus previously used by Campbell and Dulmage (4), which comprises the Scatchard equilibrium still and a barostat made up from various suggestions. The apparatus works very well, since there is no detectable fluctuation in pressure and the boiling-point fluctuation is only $\pm 0.01°$ C (at most). Equilibrium liquid and vapor phases were analyzed by density and refractive index determinations using the graphs of Reinders and de Minjer.



FIGS. 1–3. Freezing-point diagrams. System benzene–chloroform (Fig. 1); acetone–benzene (Fig. 2); chloroform–acetone (Fig. 3).

EXPERIMENTAL RESULTS

Equilibrium Diagrams

The binary systems benzene–chloroform, benzene–acetone, and chloroform–acetone are represented in Figs. 1, 2, and 3 and the ternary system in Fig. 4.

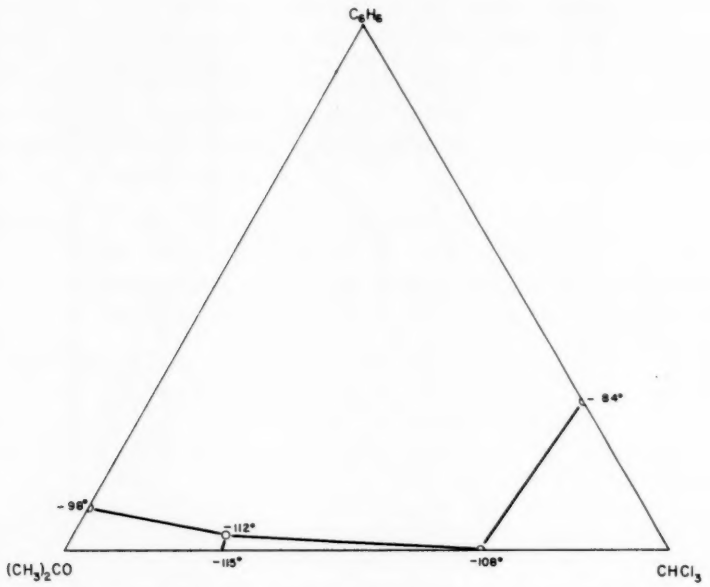


FIG. 4. Ternary freezing-point diagram of system benzene–acetone–chloroform.

Heats of Mixing

The heats of mixing of acetone–chloroform and of acetone – carbon tetrachloride have been published previously (2).

TABLE I

Heats of mixing

(*a*) Acetone–benzene			(*b*) Benzene–chloroform		
Mole fr. acetone	ΔH/mole mixture (cal)	ΔH/mole benzene (cal)	Mole fr. $CHCl_3$	ΔH/mole mixture (cal)	ΔH/mole benzene (cal)
0.230	28	41	0.218	−60	−77
0.374	40	65	0.358	−91	−140
0.492	46	91	0.455	−106	−190
0.548	46	102	0.528	−108	−230
0.618	41	107	0.598	−103	−260
0.708	30	104	0.691	−90	−290
0.829	18	108	0.817	−69	−380
			0.881	−59	−490
			0.917	−47	−570

TABLE I *(Concluded)*

(*c*) Acetone–chloroform–benzene

Mole fractions in mixtures		Mole fractions in absence of benzene		ΔH/mole mixture (cal)*
Acetone	Chloroform	Acetone	Chloroform	
	Series i. 0.1 mole fraction benzene present in all solutions			
0.799	0.101	0.887	0.113	−85
0.718	0.182	0.798	0.202	−170
0.627	0.273	0.697	0.303	−250
0.545	0.355	0.605	0.395	−330
0.450	0.450	0.501	0.499	−380
0.314	0.586	0.350	0.650	−410
0.190	0.710	0.211	0.789	−300
0.151	0.749	0.168	0.832	−290
0.106	0.794	0.118	0.882	−210
	Series ii. 0.20 mole fraction benzene present in all solutions			
0.681	0.119	0.851	0.149	−100
0.620	0.180	0.774	0.226	−170
0.506	0.294	0.632	0.368	−280
0.415	0.385	0.399	0.601	−350
0.302	0.498	0.377	0.623	−350
0.201	0.599	0.251	0.749	−320
0.095	0.705	0.119	0.881	−210
	Series iii. 0.30 mole fraction benzene present in all solutions			
0.595	0.105	0.850	0.150	−66
0.518	0.182	0.740	0.260	−160
0.441	0.259	0.630	0.370	−240
0.361	0.339	0.516	0.484	−270
0.200	0.500	0.286	0.714	−260
0.117	0.583	0.167	0.833	−220
	Series iv. 0.40 mole fraction benzene present in all solutions			
0.510	0.090	0.850	0.150	−45
0.408	0.192	0.680	0.320	−130
0.300	0.300	0.500	0.500	−190
0.208	0.392	0.347	0.653	−220
0.100	0.500	0.167	0.833	−180
	Series v. 0.50 mole fraction benzene present in all solutions			
0.384	0.116	0.768	0.232	−57
0.312	0.188	0.624	0.376	−130
0.218	0.282	0.436	0.564	−170
0.123	0.379	0.246	0.754	−180
	Series vi. 0.60 mole fraction benzene present in all solutions			
0.297	0.103	0.742	0.258	−54
0.236	0.164	0.590	0.410	−95
0.169	0.231	0.422	0.578	−120
0.107	0.293	0.267	0.733	−140
	Series vii. 0.70 mole fraction benzene present in all solutions			
0.211	0.089	0.703	0.297	−34
0.152	0.148	0.507	0.493	−68
0.091	0.209	0.303	0.697	−90
	Series viii. 0.80 mole fraction benzene present in all solutions			
0.101	0.099	0.505	0.495	−41

*These figures include the heats of mixing of the benzene with the acetone and with the chloroform.

TABLE II

Dielectric constants and apparent molar polarization of acetone–chloroform mixtures in large excess of benzene at 25° C

Composition				Molar polarization of solutions and apparent molar polarization of acetone, chloroform, or compound			
Mole fr. acetone	Mole fr. chloroform	Density ($d_4^{25°}$)	Dielectric constant	Soln.	Acetone	Chloroform	Comp.
		Series i.	Mole fraction benzene = 0.90				
0.1000	0.0000	0.8662	3.329	38.40	144.1	—	—
0.0909	0.0000	0.8668	3.250	37.33	144.1	—	—
0.0900	0.0100	0.8734	3.247	37.62	—	—	210
0.0816	0.0000	0.8677	3.159	36.87	151.8	—	—
0.0800	0.0200	0.8794	3.159	37.23	—	—	206.5
0.0722	0.0000	0.8682	2.979	35.09	157.3	—	—
0.0700	0.0300	0.8867	3.087	36.07	—	—	194.7
0.0625	0.0000	0.8691	2.917	34.47	151.7	—	—
0.0600	0.0400	0.8906	2.982	35.09	—	—	201.8
0.0526	0.0000	0.8698	2.806	33.30	153.0	—	—
0.0500	0.0500	0.8977	2.907	34.28	—	—	205.8
0.0000	0.1000	0.9258	2.456	29.02	—	50.3	—
0.0000	0.0910	0.9219	2.438	28.77	—	49.9	—
0.0100	0.0900	0.9207	2.554	30.24	—	—	226
0.0000	0.0820	0.9168	2.423	28.01	—	50.5	—
0.0200	0.0800	0.9150	2.045	31.36	—	—	217
0.0000	0.0720	0.9120	2.400	28.29	—	49.31	—
0.0300	0.0700	0.9092	2.751	32.59	—	—	221.0
0.0000	0.0630	0.9074	2.386	28.12	—	49.84	—
0.0400	0.0600	0.9030	2.833	33.50	—	—	212.8
0.0000	0.0530	0.9012	2.370	27.93	—	53.77	—
0.0500	0.0500	0.8961	2.904	34.30	—	—	206.2
		Series ii.	Mole fraction benzene = 0.95				
0.0452	0.0000	0.8698	2.733	32.50	159.7	—	—
0.0450	0.0050	0.8728	2.717	32.28	—	—	208
0.0404	0.0000	0.8698	2.687	31.98	162.6	—	—
0.0400	0.0100	0.8751	2.693	32.04	—	—	200
0.0355	0.0000	0.8703	2.632	31.33	163.1	—	—
0.0350	0.0150	0.8763	2.653	31.64	—	—	214.7
0.0320	0.0000	0.8710	2.577	30.65	156.9	—	—
0.0300	0.0200	0.8813	2.609	31.02	—	—	214.5
0.0256	0.0000	0.8712	2.537	30.18	171.1	—	—
0.0250	0.0250	0.8850	2.555	30.34	—	—	207.2
0.0000	0.0452	0.8963	2.354	27.95	—	54.89	—
0.0050	0.0450	0.8968	2.407	27.36	—	—	210.0
0.0000	0.0404	0.8942	2.343	27.57	—	54.0	—
0.0100	0.0400	0.8938	2.452	29.03	—	—	225.0
0.0000	0.0355	0.8921	2.338	27.52	—	55.57	—
0.0150	0.0350	0.8912	2.489	29.47	—	—	212.7
0.0000	0.0306	0.8915	2.324	27.20	—	51.96	—
0.0200	0.0300	0.8876	2.542	30.19	—	—	225.5
0.0000	0.0256	0.8880	2.320	27.24	—	56.25	—
0.0250	0.0250	0.8859	2.558	30.34	—	—	207.2

When the molar polarizations of acetone in benzene, in the absence of chloroform, and of chloroform in benzene, in the absence of acetone, are extrapolated to zero concentration, in the usual way, and the dipole moments calculated, using the refractive indices to calculate the distortion polarization, the following values are obtained.

Acetone 2.79 (lit. 2.70 (5))

Chloroform 0.97 (lit. 1.10 (6))

The values for the molar polarization of the "compound", that is of an equimolecular

mixture of acetone and chloroform, are necessarily difference figures and are so scattered that no extrapolation was possible. The average value was used to calculate the dipole moment, which resulted as 2.9, as against 3.76 for the sum of the dipole moments of the constituents.

TABLE III

Densities and molar volumes

Comp. of liquid (mole fr.)		Density	Exptl.	Calc.	%
Acetone	Chloroform	(g/ml)	volume	volume	deviation
0.882	0.018	0.8080_9	75.7022	75.6822	+0.026
0.768	0.032	0.8284_3	77.2322	77.2406	−0.011
0.665	0.035	0.8400_6	78.8834	78.8763	+0.009
0.552	0.048	0.8577_8	80.4641	80.5084	−0.055
0.450	0.050	0.8677_9	82.0044	82.0553	−0.062
0.349	0.050	0.8753_6	83.5993	83.6111	−0.014
0.256	0.045	0.8795_0	85.0634	85.0908	−0.032
0.164	0.036	0.8816_2	86.5763	86.5917	−0.018
0.551	0.048	0.8583_9	80.4635	80.5193	−0.069
0.552	0.048	0.8581_3	80.4478	80.5062	−0.068
0.539	0.060	0.8665_9	80.5398	80.5889	−0.061

DISCUSSION

Figures 1 and 2 show that the binary systems benzene–chloroform and benzene–acetone are of the simple eutectic type. Figure 3 shows that acetone and chloroform form a compound, stable in the solid state, but, judging from the flatness of the maximum rather highly dissociated in the molten state. Figure 4 represents the ternary freezing point diagram; it shows that the ternary eutectics occur at very small percentages of benzene. The compound characteristic of the acetone–chloroform system continues to exist in the ternary system.

The heats of mixing of acetone–chloroform mixtures with fixed benzene content are plotted in Fig. 5. It is to be noted that the curves cross at the chloroform end, as they must necessarily do, since the heats of mixing of chloroform with benzene and of acetone with benzene themselves pass through a maximum with changing benzene concentration. The maximum in the heat of mixing curve of acetone–chloroform persists in the presence of benzene, at about the same concentration of chloroform, viz. about 60 mole%, but it becomes increasingly flattened with increasing benzene content, a necessary consequence of the decrease in the ternary heat of mixing.

It is readily possible by drawing horizontals across Fig. 5 to obtain the loci of solutions having identical heat of mixing, including zero heat of mixing. The loci thus obtained have been plotted in Fig. 6.*

The curve of zero heat of mixing was of particular interest to us, since it seemed to indicate a narrow region of pseudo-ideality, in a very non-ideal system. This curve runs from pure acetone to pure benzene, with a very small chloroform content. Accordingly, we performed some rather accurate density determinations on this series of mixtures to determine whether or not the change in volume on mixing was zero. Inspection of Table III shows that this is not so and that there is always a slight but definite contraction when the components are mixed. An inspection of Table IV, which gives the boiling points of mixtures under a fixed pressure of 705.6 mm and the partial pressures as derived from

**These curves of equal heat effect might perhaps be called "idemcals", a term derived from the Latin, since the Greek term "isotherm" has a different and well-known meaning.*

TABLE IV

Liquid–vapor equilibria, $P = 705.6$ mm

Liquid comp. mole fr.			Vapor comp. mole fr.			Partial pressure calc. by Raoult's law (P')			Exp. partial pressure (P'')			Ratio = P''/P'			Temp. (°C)
$(CH_3)_2CO$	$CHCl_3$	C_6H_6	$(CH_3)_2CO$	$CHCl_3$	C_6H_6	$(CH_3)_2CO$	$CHCl_3$	C_6H_6	$(CH_3)_2CO$	$CHCl_3$	C_6H_6	$(CH_3)_2CO$	$CHCl_3$	C_6H_6	
0.891	0.015	0.094	0.936	0.007	0.057	648.5	9.4	30.8	660.4	4.9	40.2	1.018	0.521	1.305	55.03
0.803	0.028	0.169	0.869	0.011	0.120	609.4	18.2	57.7	613.2	7.8	84.7	1.006	0.429	1.468	56.18
0.704	0.032	0.264	0.823	0.016	0.161	556.0	21.7	94.4	620.7	11.3	113.6	1.116	0.521	1.203	57.35
0.542	0.039	0.419	0.744	0.027	0.228	450.9	27.8	158.4	525.0	19.0	160.9	1.164	0.504	1.016	58.98
0.469	0.048	0.483	0.709	0.027	0.264	419.8	36.9	197.4	500.3	19.1	186.3	1.192	0.518	0.944	61.14
0.319	0.048	0.633	0.672	0.027	0.301	309.6	40.0	276.9	474.2	19.1	212.4	1.532	0.478	0.767	63.63
0.124	0.048	0.828	0.622	0.035	0.343	144.6	48.0	450.4	438.9	24.7	242.0	3.035	0.515	0.537	69.38
0.128	0.038	0.834	0.300	0.038	0.662	154.0	39.2	468.9	211.7	26.8	467.1	1.375	0.684	0.996	70.36

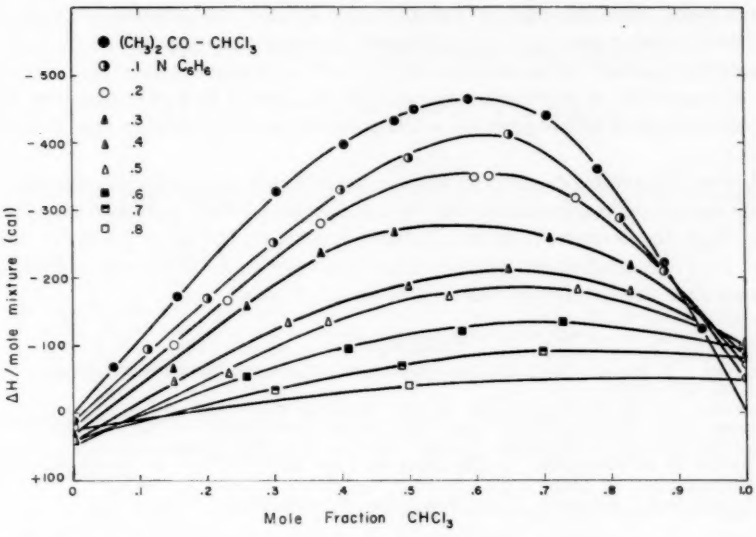


FIG. 5. Heat of mixing per mole of mixture vs. mole fraction of chloroform. Mole fraction calculated for the absence of benzene.

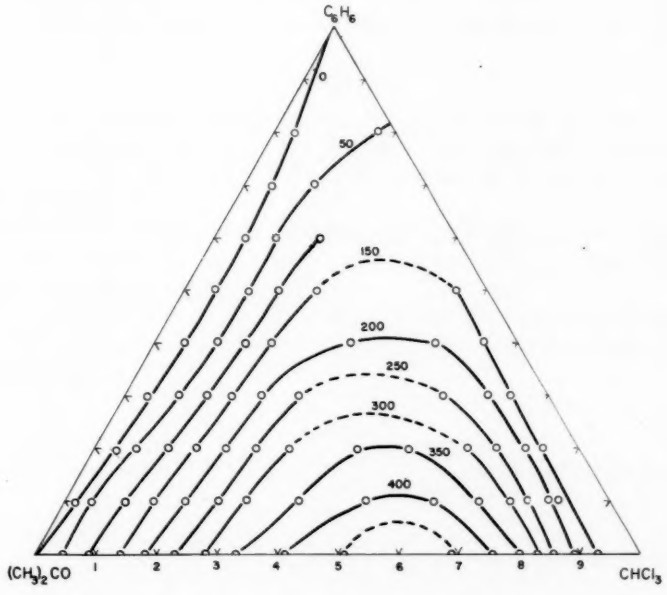


FIG. 6. Curves of equal heats of mixing. Figures on curves give the heat of mixing in negative calories.

Raoult's law and as calculated from the vapor composition, shows that these solutions are far from being ideal. It appears then that this series of solutions is not even pseudo-ideal and that the zero heat of mixing is merely a result of compensating factors.

The dielectric-constant measurements show that the dipole moment of the compound, or rather of a solution of equimolar proportions of acetone and chloroform in benzene, is greater than those of either acetone or chloroform, but considerably less than the sum of the two.

Since it was not possible to extrapolate our measurements to infinite excess of acetone or chloroform, our values must all refer to a compound which is highly dissociated. In view of the high dipole moment of the dissociated acetone, the figure given for the dipole moment of the compound is certainly too high and must be considered as purely qualitative evidence that the compound exists in benzene solution.

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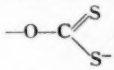
INFRARED SPECTRA OF XANTHATE COMPOUNDS

II. ASSIGNMENT OF VIBRATIONAL FREQUENCIES[1]

L. H. LITTLE,[2] G. W. POLING,[3] AND J. LEJA[3]

ABSTRACT

Discrepant interpretations regarding the frequency of the C=S stretching mode are reviewed and assignments of frequencies for the vibrational modes of the xanthate group,  , are presented.

A band at 1020–1070 cm^{-1} is assigned to the C=S stretching mode. Bands at 1200 cm^{-1} and 1110–1140 cm^{-1} are ascribed to the stretching vibrations of the C—O—C linkage.

The effects of the alkyl hydrocarbon chain length and of metal atoms (alkali metals, copper, and zinc) in displacing some of the frequencies are recorded.

In studying adsorption of xanthates on metals and their sulphide minerals by infrared spectroscopy, it became necessary to assign the spectral frequencies to the vibrational modes of the xanthate group. Previous studies of the spectra of xanthates (1, 2) and similar compounds (3, 4) were mainly exploratory in nature, due largely to the uncertain assignment of the C=S stretching mode for thiocarbonyl compounds (5, p. 293; 6; 7), in general.

Spectra of xanthates and similar compounds have been recorded and compared with recent studies of the thiocarbonyl stretching vibration (8, 9). Assignments of the xanthate vibrational frequencies have been made and conclusions reached with respect to the structures of dixanthogens, heavy metal xanthates, and alkali metal xanthates.

PROCEDURE

The spectra were recorded on Perkin–Elmer 21 and 221 double beam infrared spectrophotometers using sodium chloride prisms and on a Beckman IR4 infrared spectrophotometer using a cesium bromide prism. The solid samples were studied as mulls in nujol or in hexachlorobutadiene.

The intensities of the bands given in Table III, measured with the cesium bromide prism, are directly comparable with those of the bands shown in Figs. 1–4 for spectra measured with the sodium chloride prism.

The Raman spectrum of $(n\text{-}C_4H_9\text{—}S)_2C\text{=}O$ was recorded on a Cary Raman spectrophotometer. The other compounds are colored and, thus, are unsuitable for study by Raman spectroscopy.

*(1) Xanthates**

Potassium xanthate homologues, $C_nH_{2n+1}\text{—}O\text{—}C(=S)\text{—}SK$, listed in Table I, were prepared

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Contribution from the Division of Applied Chemistry, National Research Council, Ottawa, Canada, and the Department of Mining and Metallurgy, University of Alberta, Edmonton, Alberta.

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**The dotted bands shown in Fig. 1 occur where bands due to the compounds being studied are masked by those of the nujol mulling agent.*

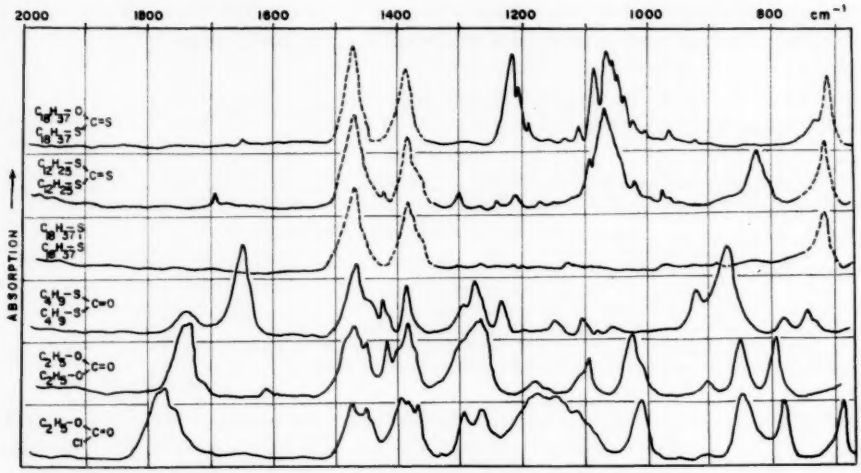


FIG. 1. Selected carbonyl and thiocarbonyl compounds.

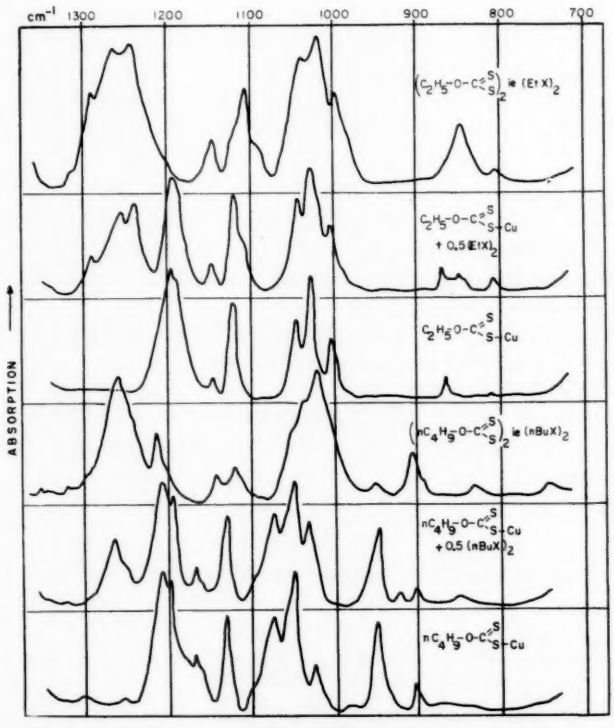


FIG. 2. Ethyl and butyl xanthates of copper and dixanthogens.

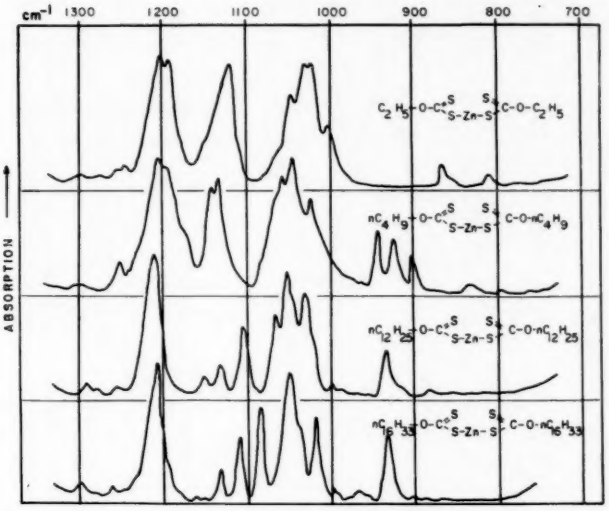


FIG. 3. Zinc alkyl xanthates.

TABLE I
Analysis of xanthates

Potassium salt of alkyl xanthate	% C		% H		% S	
	Calc.	Chem. anal.	Calc.	Chem. anal.	Calc.	Chem. anal.
K-methyl xanthate	16.45	16.38	2.07	2.10	43.84	43.59
K-ethyl xanthate	22.48	22.62	3.14	3.20	40.01	38.04
K-*n*-propyl xanthate	27.56	27.14	4.05	4.01	36.79	36.50
K-*n*-butyl xanthate	31.89	30.97	4.82	4.63	34.05	33.19
K-*n*-amyl xanthate	35.61	34.79	5.48	4.78	31.69	28.83
K-*n*-hexyl xanthate	38.85	38.78	6.05	6.04	29.73	29.40
K-*n*-nonyl xanthate	46.47	46.53	7.41	7.35	24.81	23.77
K-*n*-cetyl xanthate	57.25	55.63	9.32	9.15	17.98	17.86

as described previously (1).

AnalaR grade cupric sulphate and zinc sulphate were used to prepare heavy metal xanthates from solutions of alkali xanthates. It has been shown previously (1) by spectroscopic methods that dixanthogen is produced during the precipitation of copper xanthate from solutions of cupric salts, while no dixanthogen is produced during the precipitation of zinc xanthate. These findings are now confirmed by analytical results (see Table II).

(2) S,S-di-n-butyl Dithiocarbonate $n\text{-}C_4H_9\text{—}S$ $C{=}O$ $n\text{-}C_4H_9\text{—}S$

The dithiocarbonate was prepared by the method described by Bulmer and Mann (10). Phosgene was passed through a solution of sodium *n*-butyl mercaptide in ethanol

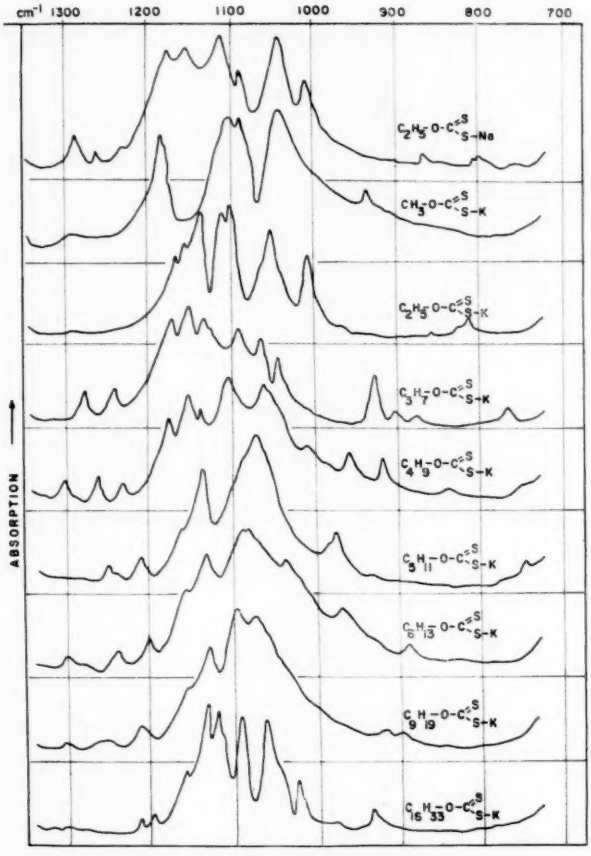


FIG. 4. Alkali metal xanthates.

and the resulting material was fractionally distilled (133° C at 20 mm Hg). Analysis: Calculated: 52.38% C; 8.79% H; 31.08% S. Found: 52.35% C; 8.75% H; 31.17% S.

*(3) S,S-didodecyl Trithiocarbonate** $n\text{-}C_{12}H_{25}\text{—}S$, $n\text{-}C_{12}H_{25}\text{—}S$, $C{=}S$

Analysis: Calculated: 67.20% C; 11.28% H; 21.53% S. Found: 67.93% C; 11.15% H; 19.40% S.

(4) O,S-dioctadecyl dithiocarbonate† $n\text{-}C_{18}H_{37}\text{—}O$, $n\text{-}C_{18}H_{37}\text{—}S$, $C{=}S$

*Sample from B.D.H., Poole, England.
†Sample provided by D.S.I.R., Warren Spring Laboratory, Stevenage, Herts, England.

TABLE II

Analysis of Zn and Cu xanthates

Material	Formula for calculations	% C		% H		% S		% metal	
		Calc.	Chem. anal.	Calc.	Chem. anal.	Calc.	Chem. anal.	Calc.	Chem. anal.
Zinc *n*- butyl xanthate	$(n\text{-}C_4H_9\text{—O—C}(=S)\text{—S})_2Zn$	33.00	33.21	4.98	5.19	35.25	34.80	% Zn 17.97	% Zn 18.03
Copper *n*-butyl xanthate	$(n\text{-}C_4H_9\text{—O—C}(=S)\text{—S})_2Cu$ (cupric)	33.17		5.01		35.43		% Cu 17.55	% Cu
	$n\text{-}C_4H_9\text{—O—C}(=S)\text{—S—Cu}$ (cuprous)	28.22		4.26		30.14		29.86	
Ether-extracted copper xanthate precipitate			28.67		4.26		29.79		28.37
Non-extracted fresh precipitate			33.07		5.11		35.02		18.44
Mixture of 2:1 moles cuprous xanthate–dixanthogen (calculated)		33.17		5.01		35.43		17.55	

The original sample has been purified by Al_2O_3 column chromatography and gave the following analysis: Calculated: 74.18% C; 12.45% H; 10.70% S. Found: 73.80% C; 12.00% H; 10.97% S.

(5) Dialkyl Carbonates

Dialkyl carbonates (ethyl, *n*-butyl, and *n*-amyl) were commercial high-purity reagents.

(6) Alkyl Chloroformates

Alkyl chloroformates (ethyl and *n*-butyl) were commercial high-purity reagents.

INFRARED SPECTRA OF CARBONYL AND THIOCARBONYL COMPOUNDS

C=S Stretching Mode

Figure 1 shows the spectra of thiocarbonate compounds of the types R—O—C(=S)—S—R and $(RS)_2C{=}S$. It is seen that spectra of both types of compounds have strong bands at 1060–1070 cm^{-1}. Intense bands in this region are absent in molecules which do not contain the C=S group, although some weaker bands appear in this region for diethyl carbonate and ethyl chloroformate (Fig. 1).

The shape of the band at 1060 cm^{-1} is similar throughout the series of spectra of molecules containing the C=S group (Figs. 1, 2, and 3) and is composed of several peaks. This band has been assigned to the C=S stretching mode.

The C=S stretching mode has been assigned over a wide range of frequencies by different workers. Jones *et al.* (11) have discussed the variation of frequencies, depending on the environment of the C=S group, over the range 1000–1400 cm^{-1}. Hazeldine and Kidd (6) assigned to the C=S stretching vibration a band at 1050–1120 cm^{-1} in the spectra of the compounds $(RO)_2C{=}S$ and $(RS)_2C{=}S$, while Marvel *et al.* (7) assigned to this vibration a band at 1170–1195 cm^{-1}. Recently, Mecke *et al.* (8, 9) have investigated the spectra of a considerable number of molecules containing the C=S group and they ascribed its stretching frequency to the range 1053–1234 cm^{-1}; in the trithiocarbonate compounds the range was 1050–1060 cm^{-1}. An extremely intense absorption band between 1110 and 1145 cm^{-1} in the spectra of two mercaptopyridines has been assigned by Spinner (12) to the stretching vibration of conjugated C=S groups.

Felumb (3, 4) studied the spectra of many thiocarbonate molecules and assigned the C=S stretching mode to a band occurring at 1200–1250 cm^{-1}. The series of compounds studied by Felumb was, however, incomplete insofar as the compounds $(RS)_2C{=}S$ and $(RS)_2C{=}O$ were omitted. The former molecule, which contains the C=S group, has no strong absorption band in the region 1200–1250 cm^{-1} (Fig. 1). Moreover, all the molecules studied by Felumb contained the C—O—C linkage, which would be expected to show strong absorption bands at about 1200 cm^{-1} (5, p. 161). The molecule $(RS)_2C{=}O$, which has neither C—O—C nor C=S groups, has no strong bands between 1000 cm^{-1} and 1300 cm^{-1} (Fig. 1).

C—O—C Stretching Modes

Thompson and Torkington (13) have assigned two bands in the region of 1200 cm^{-1} to the stretching of the C—O bonds in esters. The assignment of absorption bands in the range 1000–1200 cm^{-1} in molecules containing the C—O—C group has been discussed

by Hales *et al.* (14). Their conclusion was that the two bands in this region may be associated with the stretching vibrations of the C—O—C group.

The spectra of copper and zinc xanthates, dixanthogens, and O,S-dioctadecyl xanthate (Figs. 1, 2, and 3) show two bands in the region 1100–1250 cm^{-1}: an intense band at 1200–1250 cm^{-1} and a weaker band at 1110–1140 cm^{-1}. The latter band is of variable intensity, being sensitive to the length of the hydrocarbon chain and the nature of the metal atoms incorporated in the compounds. It can be seen from the spectra of the zinc alkyl xanthates (Fig. 3) that the intensity of this band decreases as the chain length increases.

In the spectra of ethyl and *n*-butyl dixanthogens (Fig. 2), the frequency of the intense band is shifted to 1250 cm^{-1} (from 1200 cm^{-1} for copper and zinc xanthates) and the intensity of the band at lower frequency (1110 cm^{-1}) is greatly decreased for the dixanthogens. These bands appear at 1220 cm^{-1} and 1110 cm^{-1} for O,S-dioctadecyl xanthate (Fig. 1).

The spectra of compounds which do not contain the C—O—C linkage, i.e., $(RS)_2C{=}O$ and $(RS)_2C{=}S$ (Fig. 1) do not have strong bands between 1100 cm^{-1} and 1250 cm^{-1}.

The spectra of ethyl chloroformate and diethyl carbonate (Fig. 1) show the intense high-frequency bands at 1160 cm^{-1} and 1260 cm^{-1}, respectively, for these two compounds, and a considerably weaker band at a lower frequency, 1020 cm^{-1}. This band is weaker than the intense band ascribed to the C=S stretching mode of xanthates.

The bands at 1120 cm^{-1} and 1200 cm^{-1} appearing in the spectra of xanthates are here ascribed to the stretching vibrations of the C—O—C linkage.

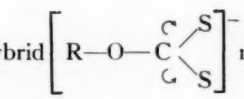
C=O Stretching Mode

The intense band at 1650–1780 cm^{-1}, which occurs in the spectra of compounds containing the C=O group, viz. dialkyl carbonates, alkyl chloroformates, and $(n\text{-}C_4H_9S)_2C{=}O$, (Fig. 1), is absent from the spectra of trithiocarbonate and of all the xanthate compounds. This band has been ascribed to the C=O stretching mode of the carbonyl compounds.

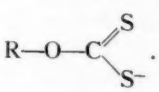
In addition to the carbonyl absorption of $(n\text{-}C_4H_9S)_2C{=}O$, which occurs as a very intense band at 1650 cm^{-1} (Fig. 1), a weaker band is found at 1750 cm^{-1}. This is probably an overtone or combination band of the intense bands at 870 cm^{-1} and 920 cm^{-1}.

Structure of Xanthates

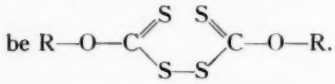
The spectra of copper and zinc xanthates (Figs. 2 and 3) show well-defined bands at 1200 cm^{-1} and 1120 cm^{-1}, which have been attributed to vibrations of the C—O—C linkage, while the intense band at 1060 cm^{-1} has been assigned to the C=S stretching mode.

The resonance hybrid  may be considered to represent the structure of

the metal xanthates (2). However, the xanthate esters (Fig. 1), which do not exist as resonance hybrids, have the same C=S band at 1060 cm^{-1} as all the heavy metal xanthates. Consequently the structure of the heavy metal xanthates must be

 .

For similar reasons the structure of the dixanthogens, retaining the C=S group, must

be  .

C—S and S—S Stretching Modes

Intense absorption bands occur at 830 cm^{-1} and 870 cm^{-1} in the spectra of $(n\text{-}C_{12}H_{25}S)_2C{=}S$ and $(n\text{-}C_4H_9S)_2C{=}O$ respectively (Fig. 1), while a band of medium intensity appears at 850 cm^{-1} in the spectrum of ethyl dixanthogen (Fig. 2). The intensities of the bands for $(n\text{-}C_4H_9S)_2C{=}O$ and ethyl dixanthogen are far greater than those of bands at lower frequencies (Table III). It is probable, therefore, that the bands at lower frequencies are associated with fundamental vibrations and not with overtones or combinations. An intense band also occurs at 870 cm^{-1} in the Raman spectrum of $(n\text{-}C_4H_9S)_2C{=}O$ (Table III).

The frequencies of these bands are considerably higher in value than those usually associated with the stretching of C—S or S—S bonds. Bellamy (5, p. 290) has discussed the assignments of C—S and S—S stretching modes to weak bands in the spectrum, occurring between 600–700 cm^{-1} and 400–500 cm^{-1}, respectively.

The intense bands (830 to 870 cm^{-1}) may be associated with an asymmetric C—S stretching mode of the C—S—C—S—C chain in the molecules $(n\text{-}C_{12}H_{25}S)_2C{=}S$ and $(n\text{-}C_4H_9S)_2C{=}O$ or the C—S—S—C chain in ethyl dixanthogen. It must be noted, however, that the disulphide $(n\text{-}C_{18}H_{37}S)_2$ (Fig. 1) does not have an intense absorption band in this region. Moreover, the metal xanthates, which have only one C—S bond also show bands in the region 800–950 cm^{-1} (Figs. 2 and 3), although these bands are generally weaker than those discussed above.

Jones *et al.* (11) have tentatively assigned bands occurring at 880–700 cm^{-1} in the spectra of "carbon sulphoxy chloride" and dimeric thiocarbonyl chloride to the stretching of the C—S bond. It is possible that, due to the environment of the C—S bond in the xanthate group, the frequency of the C—S stretching mode may be raised above the normal limits discussed by Bellamy.

An intense band appearing at 600 cm^{-1} in the Raman spectrum of $(n\text{-}C_4H_9S)_2C{=}O$ is probably due to a C—S stretching mode of this compound (5, p. 290).

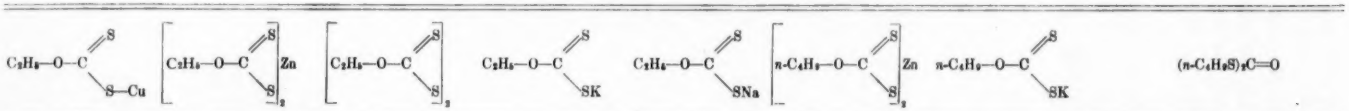
Several bands appear between 300 and 550 cm^{-1} in the spectra of xanthates (Table III). Although the spectrum of ethyl dixanthogen has more bands in this region than those of the metal xanthates, no definite assignment can be given to the S—S stretching mode of dixanthogens.

Precipitation of Copper Xanthate

Pearson and Stasiak (2) have published spectra of potassium xanthates, heavy metal (Cu, Pb, Zn) xanthates, and potassium oxyxanthates $C_nH_{2n+1}—O—C(=O)—SK$. In general, their spectra of corresponding xanthates are identical with those shown previously (1) and with those reported here. However, their spectrum of cupric xanthate corresponds to our spectrum of cuprous xanthate. The latter material was obtained after washing off the dixanthogen, which was coprecipitated with cuprous xanthate during the addition of cupric salts to solutions of alkali xanthates (1).

TABLE III

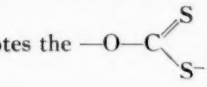
Cesium bromide infrared and Raman spectra of thiocarbonates



																				Infrared spectrum			Raman spectrum	
ν*	Δν½†	% A‡	ν	Δν½	% A	ν	Δν½	% A	ν	Δν½	% A	ν	Δν½	% A	ν	Δν½	% A	ν	Δν½	% A	ν	Δν½	% A	ν	% A
									290	~4	6													170	8
300	9	8				312	~25	7	308	9	15	308	~10	10	308	10	26	~295	~10	sh					
			345	~7	~20							327	2	10				~303	~5	15				220	11
350	9	8							350	~5	2							395	~10	3				440	8
			360	~15	~20	380	17	14							390	10	9				475	7	3		
453	9	10	452	10	18	425	13	11	447	8	29				405	11	18	435	9	20					
						470	15	3				470	~90	55	500	9	17	505	7	16	573	10	11	600	40
547	10	8				525	15	5	540	~15	2							~670	~10	~3				660	24
						565	10	2										750	10	~4					
667	~10	6	655	10	9	647	~25	6	655	~15	10	620	~60	30	665	10	10				747	~25	17	740	17
						673	~20	6										842	~10	~3					
						695	~15	8	672	~20	9				740	8	18				790	~20	11	800	12
815	~10	4	820	~10	7	815	17	15	820	~10	9	805	~15	6				925		13					
									840	~15	2	850	~10	2	840	~	2	962		11	870	~30	86	870	21
873	10	13	875	~15	11	850	22	41	875	~10	2	865	~10	3	904	10	12				920	~15	35	900	19
															927	7	13	1065		70					
															945	8	37				1050	20	7	1060	24
1015		43							1015		43							1107		78	1080	10	4		
															1026		38	1153		70	1105	10	11	1100	24
1040		80	1035		78	1020		~90				1040		74	1040		93				1147	15	11		
1053		37							1055		75										1235	15	17	1220	12
									1107		78										1280	15	24	1280	17
1127		66	1130		72	1110		67	1122		78	1115		74	1135		70				1300	~20	13	1310	25
						1153		31	1145		79	1153		70	1210		90				1345	~10	4		
1200		82	1213		80	1245		~90				1170		69							1387	10	15		
																					1420	10	18	1420	43
																					1470	~25	37	1460	64
																					1650	17	78	1650	44
																					1737	~40	20	1750	6

*Band frequency (cm^{-1}).
†Half-band width (cm^{-1}).
‡% absorption at band maximum.

Pearson and Stasiak do not state whether their copper xanthate precipitate was washed with solvents, yet in their spectrum no band appears at 1250 cm^{-1}, characteristic of dixanthogen in the precipitate. Nor do they state whether their elemental analysis was made before or after washing with solvents. Results of the analysis of the precipitate both before and after ether extraction are shown in Table II. In the absence of knowledge that the precipitate was a mixture of cuprous xanthate and dixanthogen, the results would indicate that it was cupric xanthate.

Infrared spectra (Fig. 2) and chemical analysis (Table II) suggest that the reaction between cupric ions and xanthate ions results in the coprecipitation of cuprous xanthate and dixanthogen in the molar ratio 2:1; $4\ RX^- + 2\ Cu^{++} \rightarrow 2\ RXCu + (RX)_2$ where X^- denotes the  group. With zinc ions a zinc dixanthate, but no dixanthogen, is formed.

Alkali Metal Xanthates

Spectra of some alkali metal xanthates are shown in Fig. 4. The absorption bands in the region 1000–1200 cm^{-1} are not well resolved but it is possible to distinguish three more or less distinct groups of bands, corresponding to the bands at 1200 cm^{-1}, 1130 cm^{-1}, and 1060 cm^{-1} for the heavy metal xanthates in Figs. 2 and 3.

If such a grouping of bands in the spectra of alkali metal xanthates is accepted, then the frequencies of the C—O—C linkage, discussed earlier, would appear to be displaced to lower values than those given for the C—O—C linkage in the heavy metal xanthates. The frequency of the band assigned to the C=S stretching mode varies from 1040 to 1080 cm^{-1} in the spectra of alkali metal xanthates. The presence of this band suggests that the C=S bond is preserved in the structure of the alkali metal xanthates.

Acknowledgments

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STUDIES ON CHLOROBIUM CHLOROPHYLLS

II. THE RESOLUTION OF OXIDATION PRODUCTS OF CHLOROBIUM PHEOPHORBIDE (660) BY GAS–LIQUID PARTITION CHROMATOGRAPHY[1]

H. V. Morley[2] and A. S. Holt

ABSTRACT

Methylethylmaleimide, methyl-*n*-propyl maleimide, and dihydrohematinic acid imide are obtained from *Chlorobium* pheophorbide (660) on chromic acid oxidation. The separation and isolation of these products and of other imides and pyrroles by gas–liquid partition chromatography is described.

INTRODUCTION

It has been reported that *Chlorobium* chlorophyll (660) gives a negative Molisch phase test and fails to undergo methanolysis with ring opening (1). These observations and others to be published shortly indicate that this pigment differs from other known chlorophylls. An investigation involving degradation of the molecule to identifiable, substituted monocyclic compounds corresponding to the original pyrrole nuclei was therefore undertaken.

Each of the degradative methods described in the literature has disadvantages. Reduction by hydriodic acid (2) greatly complicates the analytical problem since each nucleus can yield up to four different pyrroles. Oxidation by chromic acid (3), while theoretically producing one imide per nucleus, causes loss of nuclei which possess unstable β-groups, e.g. vinyl, formyl, and hydroxyethyl groups (4). In this laboratory, oxidation by permanganate (5) gave yields of pyrroledicarboxylic acids which were too low to permit their isolation for elementary analysis.

Oxidation by chromic acid was chosen as the most suitable method of degrading *Chlorobium* pheophorbide (660). For the resolution of the resulting mixture of imides, gas–liquid partition chromatography (GLPC) required less starting material and proved to be faster and more convenient than previously described methods (3, 4, 6, 7, 8). A study of the separation of synthetic and analytical pyrroles by GLPC was initiated (Table I) but discontinued when imides were shown to be separable by the same technique (9).

TABLE I

Retention volumes of pyrroles at 180°
relative to that of 2,4-dimethylpyrrole = 1

Pyrrole	0.50
2-Methylpyrrole	0.69
2,4-Dimethylpyrrole	1.00
3-Methyl-4-ethylpyrrole (opsopyrrole—fraction 1)	1.56
2,4-Dimethyl-3-ethylpyrrole (cryptopyrrole—fraction 2)	2.18
2,3-Dimethyl-4-ethylpyrrole (hemopyrrole—fraction 3)	2.48
2,4,5-Trimethyl-3-ethylpyrrole (phyllopyrrole—fraction 4)	3.38

Oxidation of *Chlorobium* pheophorbide (660) yielded "neutral" and "acid" fractions. The chromatogram of the "neutral" fraction (Fig. 1) shows two major peaks (4 and 5)

[1]*Manuscript received November 28, 1960.*
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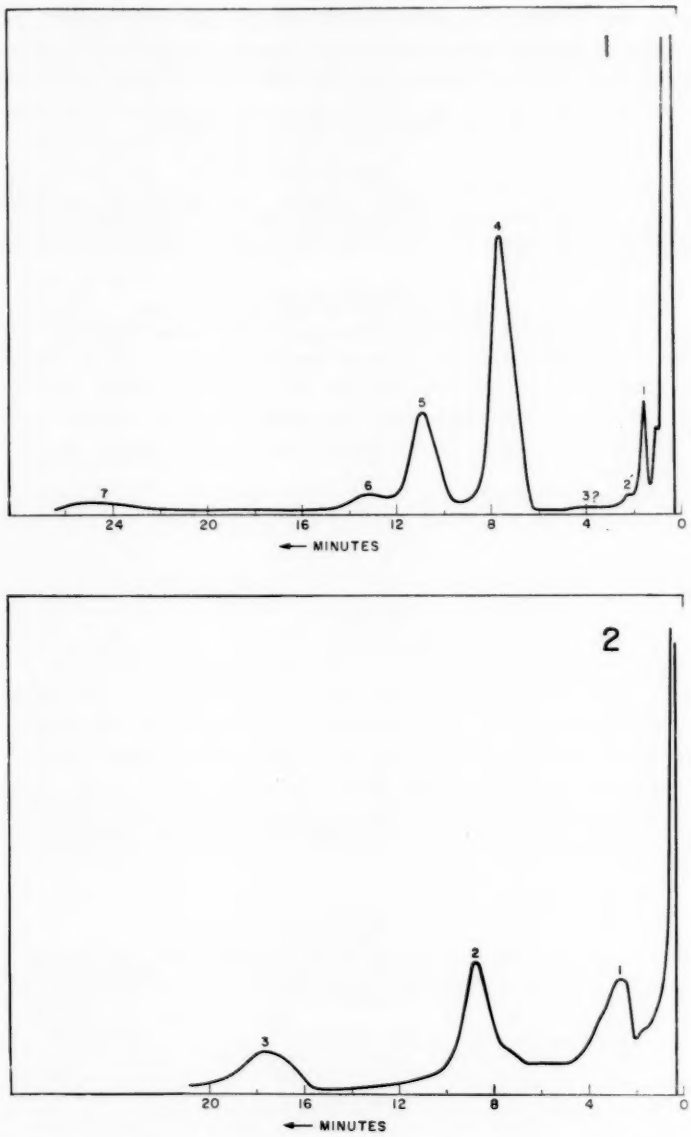


FIG. 1. Gas–liquid partition chromatogram of the "neutral" fraction from *Chlorobium* pheophorbide (660).

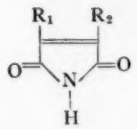
FIG. 2. Gas–liquid partition chromatogram of the "acid" fraction from *Chlorobium* pheophorbide (660).

and several minor ones. The compound responsible for peak 4 was readily shown, by GLPC, to be methylethylmaleimide by comparison with an authentic sample prepared from mesoporphyrin IX. From the retention volume (R_v, Table II), the compound

TABLE II

Retention volumes of maleimides at 200° relative to that of quinoline = 1

Maleimide	0.22	Methyl-*n*-propylmaleimide (III)	0.84
Citraconimide (I)	0.30	Bromocitraconimide	1.00
Succinimide	0.53	Hematinic acid imide methyl ester (IV)	2.90
Methylethylmaleimide (II)	0.59	Dihydrohematinic acid imide methyl ester	3.03



		R_1	R_2
I	Citraconimide	H	CH_3
II	Methylethylmaleimide	CH_3	C_2H_5
III	Methyl-*n*-propylmaleimide	CH_3	C_3H_7
IV	Hematinic acid imide	CH_3	$(CH_2)_2COOH$

responsible for peak 5 could be assumed to contain one more methylene group than methylethylmaleimide. This assumption was confirmed by elementary analysis. The melting point agreed with that of methyl-*n*-propylmaleimide (10); this structure was also deduced from the proton magnetic resonance spectrum. Subsequently, a synthetic sample of methyl-*n*-propylmaleimide (10) proved to be identical with the analytical sample. It is of interest to note that this is the first time a *n*-propyl side chain has been found in a natural tetrapyrrole.

The chromatogram of a small sample of the methylated "acid" fraction is given in Fig. 2. The products responsible for each of the three main peaks have infrared spectra not unlike those of methylethyl- and methyl-*n*-propylmaleimide. Because no reference specimen was available, dihydrohematinic acid imide was not identifiable among the products. It was thus necessary to isolate it from the remaining "acid" fraction by partition chromatography on silica gel. The eluent samples which were acidic and gave a positive imide test (11, 12) were combined and converted to the benzylamine salt. Analysis, melting point, and infrared spectrum confirmed that the product was the salt of *trans*-dihydrohematinic acid imide obtained previously by Linstead *et al.* (6). The above salt was converted to the free acid and esterified with only a slight excess of diazomethane. Such care was necessary in order to eliminate the possibility of methylating the imide nitrogen atom (13). The infrared spectrum of the colorless oil obtained after removing the solvent and excess diazomethane still showed the NH absorption band at 3390 cm^{-1} indicative of the intact imide nitrogen. A sample subjected to GLPC showed that dihydrohematinic acid imide methyl ester was responsible for peak 3 ($R_v = 3.03$) of Fig. 2. This result was to be expected since hematinic acid imide methyl ester has an R_v value of 2.90 (Table II). The substances responsible for peaks 1 and 2 were not recovered in sufficient quantity, after purification by GLPC, to permit their identification.

The above results identify at least three of the four pyrrole nuclei present in *Chlorobium* pheophorbide (660). Recent studies have shown that *Chlorobium* pheophorbide (650) possesses a hydroxyethyl group which is readily oxidized to an acetyl group, and that *Chlorobium* pheophorbide (660) possesses a similar group (14). Until these studies have been completed, the nature of the fourth nucleus in *Chlorobium* pheophorbide (660) remains in question.

EXPERIMENTAL

The preparation and purification of *Chlorobium* pheophorbide (660) from *Chlorobium* chlorophyll will be outlined in a forthcoming publication. Mesoporphyrin IX was obtained from hemin by a standard procedure (15, 16). Except where stated otherwise, infrared spectra were determined in chloroform on a Perkin–Elmer Model 21 double-beam instrument. Melting points were determined on the Koffler Hot Stage. The instrument used for GLPC was a modified Podbelniak "Chromacon" (Series 9475-3V) described previously (17). Pyrroles were separated on a column (8 ft long, 7-mm I.D.) packed with a mixture (1:4 w/w) of Apiezon M and alkali-washed Celite 545 (60–80 mesh). The operating temperature was 180° C; the carrier gas was helium with a flow rate of 75 ml/minute. The number of theoretical plates was 1300. Imides were separated as described earlier (9). The proton magnetic resonance spectrum of methyl-*n*-propylmaleimide was recorded at 60 Mc/s with a Varian V-4032 high-resolution spectrometer.

Oxidative Degradation of Chlorobium Pheophorbide (660)

The oxidation procedure and the separation of the imides into "neutral" and "acid" fractions followed closely the directions of Linstead *et al.* (6). *Chlorobium* pheophorbide (1.0 g) was dissolved in sulphuric acid (70 ml, 50% v/v); the solution was then diluted with ice (70 g) and cooled to −10° C. Chromic acid (3.3 g) in water (30 ml, 0° C) was added dropwise with stirring during 1 hour. The solution was maintained at −10° C for 2 hours with continued stirring. By this time carbon dioxide evolution had diminished. The mixture was allowed to warm slowly to room temperature with stirring until a total of 5 hours had elapsed since the first addition of chromic acid. The mixture was then extracted and fractionated (6). Later work showed that after a total period of 3½ hours no further increases in the yields of the neutral imides were indicated by GLPC.

"Neutral" Fraction

Since fractions 1, 2, and 3 (Fig. 1) did not separate well they were not investigated intensively. ν_{max} of a crude sample of fraction 1: 3500 (m), 3375 (m), 1698 (s), 1600 (w), and 1565 (m) cm^{-1}. The R_v value (0.59) of fraction 4 agreed with that of methylethylmaleimide obtained from mesoporphyrin IX (see below). Initially 32 mg were obtained; further purification by GLPC yielded 16 mg as white blades, mixed m.p. 67–68°. The infrared spectrum was superposable upon that of an authentic sample. Found: C, 60.2; H, 6.39. $C_7H_9O_2N$ requires: C, 60.4; H, 6.52%.

Fraction 5 (ca. 13 mg) was further purified by GLPC (white needles, 6.7 mg); recrystallized (chloroform–ether), m.p. 52–54°. The yields from several oxidations were bulked. Found: C, 62.6; H, 7.38; N, 8.80. $C_8H_{11}O_2N$ requires: C, 62.7; H, 7.24; N, 9.14%. The proton magnetic resonance spectrum of a 10% (w/v) solution was consistent with the methyl-*n*-propylmaleimide structure. The following shifts, given as τ values (18) and compared to tetramethylsilane as an internal standard were observed: a broad band at 1.04 (=N*H*), a triplet at 7.57 (=C—CH_2CH$_2$—), a sharp singlet at 8.01 (=C—CH_3), six unresolved peaks at 8.47 (—CH$_2$—CH_2—CH$_3$), and at 9.02 a triplet (—CH$_2$—CH$_2$—CH_3). ν_{max} (CCl_4): 3430 (w), 1769 (w), and 1725 (s) cm^{-1}. On comparison with a synthetic specimen (10) this product was found to be identical with respect to mixed melting point, infrared spectrum, nuclear magnetic resonance spectrum, and X-ray powder diagram.

The small quantities of fractions 6 and 7 permitted only the examination of the infrared spectrum. ν_{max} of both were at: 3418 (w), 1768 (w), and 1720 (s) cm^{-1}.

"Acid" Fraction

A small sample (ca. 5 mg) of the acid fraction was esterified with distilled diazomethane. The R_v values of the three main products (Fig. 2) in this sample were 0.49, 1.49, and 3.03 respectively.

The remainder was partitioned on a wet silica gel column (55×2 cm) and eluted with ethyl acetate (6). Six-milliliter samples were collected (50 tubes). Paper chromatograms were developed in ethanol–NH_4OH–water (7:1:2) and sprayed with Universal indicator spray (British Drug Houses Ltd.) for acids or with an imide spray (11, 12). The results showed that tubes 4–8 contained traces of neutral imides and that tubes 8–16 contained the bulk of the acidic imides.

Tubes 8–16 were combined and evaporated to dryness. The residue was converted to the benzylamine salt(s) of the imide acid(s). Recrystallization from methanol – ethyl acetate yielded white needles. The infrared spectrum (nujol mull) had maxima at 1298 (m); 1265 (m); 1217 (m); 1190 (s); 1168 (w); 1160 (w); 888 (w); 872 (m); 823 (m); 795 (m); 772 (m); 755 (s); 741 (m); 719 (w); 696 (m); 686 (w) cm^{-1}, which agree well with data given by Linstead *et al.* (6) for the benzylamine salt of *trans*-dihydrohematinic acid imide, m.p. 158–161° (lit. 164–165° (6)). Found: C, 61.7; H, 6.97; N, 9.71. $C_{15}H_{20}O_4N_2$ requires: C, 61.6; H, 6.90; N, 9.58%. The benzylamine salt was dissolved in a little water and the free acid was extracted into ethyl acetate and ether after acidification. The extracts were combined, dried over sodium sulphate, and evaporated to dryness *in vacuo*. The free acid in the residue from the extract was carefully esterified with distilled diazomethane in ether, by dropwise addition until a faint yellow color persisted for 15 minutes. The R_v value of the resulting colorless oil was 3.03. ν_{max}: 3390 (w), 1775 (w), 1723 (s) cm^{-1}. Found: C, 54.3; H, 6.65. $C_9H_{13}O_4N$ requires: C, 54.3; H, 6.58%.

Oxidative Degradation of Mesoporphyrin IX

Mesoporphyrin IX (250 mg) was oxidized and separated into "neutral" and "acid" fractions essentially by the method of Muir and Neuberger (8). About 5 mg of the "neutral" fraction was analyzed by GLPC; the main fraction (R_v 0.59) was collected as crystals. Methylethylmaleimide was crystallized from an aqueous solution of the remainder of the "neutral" fraction (m.p. 67–68° (lit. 68° (8)). Yield, 45 mg. This sample proved to be identical (mixed melting point, R_v value, and infrared spectrum) with that obtained as crystals from the GLPC separation described above. ν_{max}: 3430 cm^{-1}, (w); 1768, (w); and 1718 (s) cm^{-1}.

Ten milligrams of the "acid" fraction was esterified with diazomethane. Three main fractions with the following R_v values were observed: (1) 0.387, (2) 1.49, and (3) 2.90 respectively. Fraction (3) was shown by comparison with an authentic sample (R_v value and infrared absorption spectrum) to be hematinic acid imide methyl ester. ν_{max}: 3430 (w), 1768 (w), and 1722 (s) cm^{-1}. Fractions (1) and (2) have not been identified. The spectra of each contained N—H bands but differed from those of other available imides in the double bond stretching region. ν_{max}: fraction (1), 1823 (w), 1758 (s), 1720 (s), 1673 (m), and 1600 (w) cm^{-1}; fraction (2), 1815 (w) (shoulder), 1762 (s), 1723 (s), and 1673 (m) cm^{-1}.

Reductive Degradation of Hemin

Hemin (250 mg, British Drug Houses Ltd.) was heated in glacial acetic acid (4.5 ml) containing hydriodic acid (5 g; s.g. 1.96) according to the method given by Willstätter and Stoll (19). Free iodine was reduced by hypophosphorous acid which was added

dropwise during ½ hour. The reaction mixture was adjusted to pH 11 (Na_2CO_3) and pyrroles were then extracted into ether. Strongly basic reduced pyrroles were removed from the ether by aqueous monosodium phosphate. The ether solution was dried (Na_2SO_4) and evaporated.

A sample of the residue from the ether solution was analyzed by GLPC and gave four main peaks, numbered 1 to 4 in the order of their emergence from the column. These products were collected as colorless oils, which darkened rapidly upon exposure to air.

Product 2 was shown to be cryptopyrrole by comparison of its R_v value (Table I) with that of an authentic sample. Product 1 was deduced to be opsopyrrole as follows: an ether solution of the reaction mixture was extracted with 12% (w/w) hydrochloric acid. This strength acid is known to remove crypto-, phyllo- and hemo-pyrrole and leave opsopyrrole in the ether phase (20). The material in the residue from the ether solution was analyzed by GLPC and gave peak 1, with only traces of the other three peaks. Product 4 was presumed to be phyllopyrrole because: (1) it gave a positive Ehrlich test only after heating (21) (products 1, 2, and 3 gave immediate positive tests at room temperature); and (2) it is reasonable to presume it would emerge last from the column since it possesses the highest molecular weight of the four pyrroles obtained from hemin. By elimination, product 3 was assumed to be hemopyrrole. It was later found that steam distillation of the pyrroles from the alkaline solution eliminated some impurities which otherwise appeared on the chromatogram.

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FURTHER STUDIES ON THE REACTION BETWEEN HALOGEN-SUBSTITUTED NITRILES AND AMINES[1]

JOHN C. GRIVAS[2] AND ALFRED TAURINS

ABSTRACT

The scope of the reaction of halogen-substituted nitriles and amines was extended by including trifluoro- and dichloro-acetonitrile. Trifluoroacetonitrile reacts easily with primary and secondary aliphatic, primary aromatic, and heterocyclic amines to give the corresponding amidines. N-Mono- and N-di-substituted dichloroacetamidines were prepared from dichloroacetonitrile and amines. Trichloroacetonitrile also affords N-substituted amidines with heterocyclic amines.

INTRODUCTION

The reaction of trichloroacetonitrile with primary and secondary amines has been investigated and discussed (1). The present work deals with the extension of the reaction, using trifluoroacetonitrile and di- and mono-chloroacetonitrile, and a variety of amines. Trifluoroacetonitrile is expected to react even faster than trichloroacetonitrile owing to the stronger inductive effect ($-I_s$) of the trifluoromethyl group. Husted (2) synthesized a series of perfluoroalkylamidines by allowing the corresponding nitriles to react with liquid ammonia in sealed tubes for 2 weeks. Reilly and Brown (3) isolated some N-methyl-, and N,N-dimethyl-perfluoroalkylamidines by treating nitriles with methyl- and dimethyl-amine at $-60°$. They assumed that aniline, being a weak base, could not produce any amidines. There are no literature data concerning the addition of amines to the carbon–nitrogen triple bond of dichloroacetonitrile.

RESULTS AND DISCUSSION

The formation of amidines from nitriles and amines depends on both the basicity of the amine and the electron deficiency of the carbon atom of the nitrile group. The mechanism of this reaction (1) implies that the more mobile the electron pair of the amino nitrogen atom, the stronger will be the interaction between the two reactive centers and the faster the reaction will go. On the other hand, the greater the electron deficiency of the carbon atom, the faster the reaction will be. Acetonitrile does not react with amines because the mesomeric effect of the nitrile group is compensated by the ($+I_s$) inductive effect of the methyl group.

$$CH_3 \rightarrow C \overset{\curvearrowright}{\equiv} N: \qquad CF_3 \leftarrow C \overset{\curvearrowright}{\equiv} N:$$

Evidence for this was obtained by conducting a series of reactions involving primary and secondary amines and four α-halogen-substituted nitriles, of decreasing inductive ($-I_s$) effect as follows:

$$F_3C{-}CN > Cl_3C{-}CN > Cl_2HC{-}CN > ClCH_2{-}CN.$$

Trifluoroacetonitrile was found to react not only with primary and secondary aliphatic but also with primary aromatic and heterocyclic amines at room temperature providing excellent yields of products in each case. Trichloroacetonitrile also afforded mono-substituted amidines when treated with 2-amino-5-methylpyridine and 2-aminothiazole

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at room temperature. The monosubstituted amidines derived from both nitriles on the basis of infrared spectroscopic studies (4, 5) exist in the imino form (I):

$$\begin{matrix} R{-}C{-}NHR' \\ \| \\ NH \end{matrix} \qquad \begin{matrix} R = Cl_3C{-},\ F_3C{-} \\ R' = \text{Alkyl or aryl} \end{matrix}$$

(I)

The inductive ($-I_s$) effect of the dichloromethyl group proved to be strong enough to promote the non-catalyzed addition of amines to the nitrile group of dichloroacetonitrile.

$$Cl_2CH{-}CN + R'{-}NH_2 \rightarrow \underset{\text{(II)}}{Cl_2CH{-}CN} \qquad \underset{\text{(III)}}{\begin{matrix} Cl_2CH{-}C{-}NHR' \\ \| \\ NH \end{matrix}}$$

$$II + R'R''NH \rightarrow \underset{\text{(IV)}}{\begin{matrix} Cl_2CH{-}C{-}NR'R'' \\ \| \\ NH \end{matrix}}$$

The amidines (III, IV) isolated were unstable owing to the acidity of the hydrogen atom of the dichloromethyl group, coupled with the basicity of the amidine system. Thus N-mono-, and N,N-di-substituted dichloroacetamidines (III, IV) partially decomposed when distilled even at 2 mm pressure in a dry nitrogen atmosphere and they could not be kept longer than a few days. On the contrary, their picrates were stable. In general, the yields of amidines were good. The results have been summarized in Table I.

TABLE I

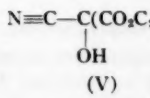
No.	Compound	Yield, %	B.p.,* °C	M.p.*	Empirical formula	Nitrogen, % Calc.	Nitrogen, % Found†
	Trifluoroacetamidines						
1	N-Ethyl-‡	90	125–126°	—	$C_4H_7F_3N_2$	20.00	19.73
2	N-Butyl-	82	39–40°/2 mm	—	$C_6H_{11}F_3N_2$	16.65	16.41
3	N-Benzyl-	91	—	51°	$C_9H_9F_3N_2$	13.86	13.78
4	N-Phenyl-§	90	—	81°	$C_8H_7F_3N_2$	14.89	14.80
5	N,N-Diethyl-‖	91	119°	—	$C_6H_{11}F_3N_2$	16.65	16.73
6	N-(5-Methyl-2-pyridyl)-	71	—	102°	$C_8H_8F_3N_3$	20.70	20.85
	Dichloroacetamidines						
7	N-Methyl-¶	55	80–85°/6 mm	—	¶	¶	¶
8	N-Piperidino-**	88	63–66°/1 mm	—	**	**	**
9	N-Phenyl	60	—	62°	$C_8H_8Cl_2N_2$	13.80	13.86
	Trichloroacetamidines						
10	N-(5-Methyl-2-pyridyl)-	81	—	83.5°	$C_8H_8Cl_3N_3$	16.64	16.66
11	N-(2-Thiazolyl)-	86	—	87°	$C_5H_4Cl_3N_3S$	17.20	17.20

*Melting points and boiling points observed, uncorrected.
†Microanalyses by W. Manser, Herrliberg, Switzerland.
‡Hydrochloride, m.p. 189–191° (decomp.). Prepared by passing hydrogen chloride gas through a solution of amidine in ether.
§Hydrochloride, m.p. 179–180° (decomp.).
‖Hydrochloride, m.p. 133–135° (decomp.).
¶Picrate, m.p. 107.5° (decomp.). Calc. for $C_9H_9Cl_2O_7$: N, 18.92%. Found: N, 18.73%.
**Picrate, m.p. 142° (decomp.). Calc. for $C_{13}H_{15}Cl_3N_4O_7$: N, 16.51%. Found: N, 16.57%.
NOTE: Picrates were prepared in benzene solution and were recrystallized from water or water–methanol mixture.

It has been reported (6) that diethylamine reacts with chloroacetonitrile in ether by substitution of chlorine to give diethylaminoacetonitrile. Experiments under various conditions confirmed these facts.

The present work has lead to the following conclusions:

(*a*) At least two strongly electronegative atoms are necessary to promote the non-catalyzed addition of amines to the nitrile group. It is of interest to note that ethyl cyanotartronate (V) adds amines in a manner identical with that of trichloro- and trifluoro-acetonitriles (7):



(V)

(*b*) Methanol cannot be used as a solvent in the reaction of trichloroacetonitrile with secondary aliphatic amines, owing to the formation of methyl trichloroacetimidate. This would also occur with trifluoro- and dichloro-acetonitrile.

(*c*) Acetonitrile is an excellent solvent.

(*d*) The reaction between primary aromatic amines and the three nitriles used in these studies does not occur in non-polar solvents.

(*e*) Primary aliphatic amines react much faster than primary aromatic amines. Secondary aliphatic amines react more slowly than primary aliphatic amines, even though the former are the stronger bases. This discrepancy can be attributed to stereochemical factors.

(*f*) Secondary aliphatic amines containing alkyl groups with more than three carbon atoms react preferentially by substitution at the α-carbon atom of trichloroacetonitrile:

$$(n\text{-}C_5H_{11})_2NH + CCl_3\text{—}CN \rightarrow (n\text{-}C_5H_{11})_2NCCl_2CN + HCl.$$

EXPERIMENTAL

A. Preparation of Trifluoroacetamidines

1. N-Butyl-α,α,α-trifluoroacetamidine.—A slow stream of trifluoroacetonitrile was passed through pure *n*-butylamine (2.9 g) in a tube which was immersed in an ice-water bath. An exothermic reaction took place. The crude product was distilled in a nitrogen atmosphere to give a colorless liquid (5.5 g, 82% yield) boiling at 39–40°/2 mm. Analysis of this compound is recorded in Table I.

2. N-Benzyl-α,α,α-trifluoroacetamidine.—In a long glass tube was placed 1.9 g of trifluoroacetonitrile (0.02 mole). The tube was cooled in a dry ice – acetone mixture and was connected by a Tygon tubing to a 100-ml pear-shaped flask containing a solution of 2.15 g (0.02 mole) of benzylamine in 10 ml of benzene. The solution was stirred by a magnetic stirrer while a slight pressure of trifluoroacetonitrile was maintained in the closed system. This was achieved by keeping the surface of the liquid trifluoroacetonitrile slightly above the surface of the cooling mixture. After ½ hour the nitrile had been used up but the stirring was continued for an additional 30 minutes. The solvent was evaporated under reduced pressure and the remaining liquid fractioned to give 3.84 g (91%) of a colorless liquid boiling at 88–90°/3 mm. In a few hours, the liquid solidified to white transparent crystals which, after two sublimations at 2 mm pressure, gave pure N-benzyl-α,α,α-trifluoroacetamidine, m.p. 51°.

3. N-Phenyl-α,α,α-trifluoroacetamidine.—A solution of 5 g of aniline in 20 ml of methanol was added to a Pyrex glass tube (20×700 mm) which was cooled in a dry ice – acetone mixture. An equimolar amount of trifluoroacetonitrile was condensed in the tube, which was then sealed and left for 4 days at room temperature. The tube was cooled to condense any unreacted trifluoroacetonitrile and opened. The reaction product was precipitated by addition of distilled water, or by evaporation of methanol at reduced

pressure, washed twice with distilled water, and dried. After sublimation the amidine (9.2 g, 91% yield) melted at 81°.

4. N,N-Diethyl-α,α,α-trifluoroacetamidine.—Equimolar quantities of trifluoroacetonitrile and diethylamine were allowed to react in a sealed Pyrex tube at room temperature for 24 hours. The mixture was then fractionated to give a colorless amidine (90% yield) boiling at 119°.

5. N-(5-Methyl-2-pyridyl)-α,α,α-trifluoroacetamidine.—Equimolar quantities of trifluoroacetonitrile and 2-amino-5-methylpyridine in acetonitrile were kept in a sealed Pyrex tube at room temperature for 4 to 6 days. The addition of water caused the separation of a liquid layer which solidified in a few minutes. The crude yellowish product was dissolved in a small volume of acetonitrile and precipitated by addition of water (yield 71%). After sublimation the amidine melted at 102°.

B. Preparation of Dichloroacetamidines

1. N-Methyl-α,α-dichloroacetamidine.—Dichloroacetonitrile (6.87 g, 0.062 mole) was added to an aqueous 25% solution of methylamine containing an equivalent amount of the amine, and the mixture was shaken for a few minutes. The lower reddish-brown layer was separated and distilled in a nitrogen atmosphere to give an almost colorless liquid (4.8 g, 55% yield) boiling at 80–85°/6 mm. Some decomposition of the product occurred during distillation and the pure amidine which was isolated turned black in 2 days.

2. Piperidino-α,α-dichloroacetamidine.—Piperidine (3.15 g, 0.037 mole) was added to a benzene solution (15 ml) of dichloroacetonitrile (4.7 g, 0.037 mole) and left at room temperature for 3 days. The mixture was then fractionated under reduced pressure in a nitrogen atmosphere to give a colorless liquid (6.4 g, 88% yield) at 63–66°/1 mm. The pure amidine changed to a black tar in 3 weeks.

3. N-Phenyl-α,α-dichloroacetamidine.—A mixture of dichloroacetonitrile (0.025 mole), aniline (0.025 mole), and 16 ml of methanol was left in a stoppered flask at room temperature for 1 week. After the evaporation of the solvent under reduced pressure a dark-brown solid was obtained. The product was then sublimed. Unreacted aniline together with a portion of the amidine was collected first but continued sublimation gave colorless N-phenyl-α,α-dichloroacetamidine (3 g, 60% yield), m.p. 62°.

C. Preparation of Heterocyclic Trichloroacetamidines

1. N-(5-Methyl-2-pyridyl)-α,α,α-trichloroacetamidine.—Trichloroacetonitrile (2.88 g, 0.02 mole) was added to a solution of 2-amino-5-methylpyridine (2.16 g, 0.02 mole) in 6 ml of acetonitrile and the mixture was left at room temperature for 4 days. Then addition of 10 ml of water caused the separation of a yellowish liquid layer which solidified in a few minutes. The compound was filtered off, and dissolved in a small volume of methanol. Addition of water to the methanol solution resulted in the isolation of a colorless product (4.1 g, 81% yield) melting at 78–79°. Sublimation at 70°/2 mm raised the melting point to 83.5°.

2. N-(2-Thiazolyl)-α,α,α-trichloroacetamidine.—This compound was prepared by a method similar to that outlined above, m.p. 87°.

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THE ABSORPTION SPECTRUM OF DIPHENYLENE IN THE NEAR-ULTRAVIOLET[1]

ROBIN M. HOCHSTRASSER

ABSTRACT

The absorption spectrum of diphenylene has been measured in the vapor at a variety of temperatures, in solution at room temperature, and in an EPA rigid glass at 90° K. From a consideration of the band structure and intensity distribution it was concluded that the weak absorption at 25,041 cm^{-1} (vapor; $f = 10^{-3}$) is due to a symmetry-forbidden electronic transition. The theoretical prediction that the excited level is of species B_{1g} was supported by the presence of a strong infrared band at 732 cm^{-1} corresponding to observed perturbing vibration of frequency 792 cm^{-1}. The solution spectrum was found to exhibit a vibrational structure typical of a g–g forbidden excitation.

The electronic levels of diphenylene are somewhat anomalous when compared to those of other alternant hydrocarbons such as the structurally similar naphthalene or phenanthrene and anthracene. The solution spectrum of diphenylene was studied by Carr, Pickett, and Voris (1) and the electronic transitions involved were subsequently classified by Clar (2, p. 279) on the basis of intensity and band position and by analogy with other alternant hydrocarbons. Recently, using the technique of mixed crystal spectroscopy the symmetry of the second molecular level, the absorption to which commences at 27,910 cm^{-1} in liquid solution, was determined (3). This level was found to belong to the $^1B_{3u}$ (long axis polarized) representation in the point group D_{2h}. Such an assignment is at variance with the systematic classification by Clar. The *p*-band, by analogy with other alternants, would involve excitation to a short axis polarized level. In view of this a closer study of the weak lower-energy band was prompted.

During the past few years the symmetry types of the molecular levels of most of the polyacenes have been determined experimentally. The theorists have correctly predicted both the symmetry and energy of these levels. However, this success is not yet known to extend to the pericondensed hydrocarbons such as pyrene and perylene or to hydrocarbons containing other than six-membered rings such as diphenylene.

There are certain features which become apparent during a qualitative examination of the absorption spectrum of diphenylene in liquid solution at room temperature. There are three obviously separated absorption regions which are taken to be due to absorption to three different electronic levels. The highest energy absorption commences at about 40,250 cm^{-1} with $\epsilon_{max} = 10^5$. This band has little structure and in both band position and intensity resembles the ^1B_b ($^1B_{2u}$) transitions of the polyacenes. The intermediate band occurs at 27,910 cm^{-1} with $\epsilon_{max} = 10^4 - 10^3$. This band resembles the ^1L_a($^1B_{3u}$) transitions of the polyacenes in these respects; however, the vibrational structure is neither regular nor similar to that observed in the ^1L_a bands of polyacenes. The lowest energy transition at 25,530 cm^{-1} with $\epsilon_{max} = 10^2$ has even lower intensity than the ^1L_b bands of benzene ($^1B_{2u}$; $\epsilon_{max} = 500$), naphthalene ($^1B_{2u}$; $\epsilon_{max} = 310$), and phenanthrene (B_1; $\epsilon_{max} = 800$).

Simple molecular orbital theory does predict that transitions to the lowest lying level of diphenylene will be forbidden by molecular symmetry. In this paper we have examined

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Contribution from the Chemistry Department, the University of British Columbia, Vancouver, B.C. This research was supported by a grant from the National Research Council of Canada.

the lowest energy band of diphenylene in the vapor and in rigid glassy solution at liquid nitrogen temperature and have obtained results which are in accord with the predictions of simple theory.

EXPERIMENTAL

Vapor Spectra

Diphenylene is a reasonably volatile solid and appreciable concentrations of vapor were obtained in a 10-cm cell at around 100° C. A small heating compartment was made which fitted into the Cary spectrophotometer (Model 14). A small crystal of diphenylene was contained in an evacuated quartz cell which could be maintained at temperatures around 100° to within 0.5°. The cell windows were always at a slightly higher temperature than the body so that no crystals could interfere with the light beam. An identical quartz path was placed in the reference beam.

Spectra at Liquid Nitrogen Temperature

The solvent used was a mixture of ether (5 parts), isopentane (5 parts), and alcohol (1 part) to be referred to as EPA. This formed an optically clear glass at the temperature of boiling nitrogen.

The low-temperature cell was constructed to fit into the sample compartment of the Cary spectrophotometer. The Dewar system was made of metal to which was fitted a copper block. The liquid was contained in a cylindrical cell with copper walls and quartz windows which fitted tightly into the copper block of the Dewar. The windows were held in by means of steel springs and the vacuum seal was obtained by pressing the windows onto indium rings. In this way spectra could be run with a perfect optical path at any temperature between 25° C and −190° C. The window assembly used was a modification of that described by Willis (4). The cell thickness was 0.33 cm. In calculating extinction coefficients at liquid nitrogen temperature correction was made for the contraction of the solution on cooling from room temperature.

The wavelength scale of the Cary was calibrated absolutely to within 2 Å in the spectral region which was covered. Often the peaks were sharp enough such that wavelength differences could be measured to ±0.4 Å, which corresponds to ±2.5 cm^{-1} at 4000 Å and ±3.1 cm^{-1} at 3600 Å. The Cary was used with a maximum slit width of 0.015 mm.

RESULTS

Vapor Spectrum

The spectrum of diphenylene vapor at two temperatures is shown in Fig. 1. The main features are as follows:

(1) The weak band system is superimposed on the long wavelength tail of the 3600 Å transition.

(2) Although not well resolved by the instrument, the spectrum at 95° C appears as a typical electronic band system with some indication of red shading.

(3) At higher temperature the very weak member at 3880 Å has gained in relative intensity. Above 125° C all the diphenylene in the cell had vaporized and further temperature increases had little effect apart from broadening and an over-all intensification of the spectra due to an increase in the hot-band intensity from the higher energy transition.

(4) No accurate vapor pressure data were available for diphenylene so it was not possible to measure extinction coefficients or oscillator strengths.

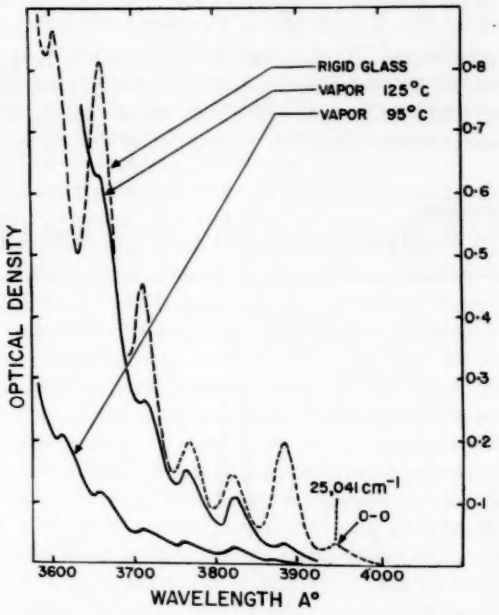

FIG. 1. The absorption spectra of diphenylene in vapor and rigid glass: the lowest energy transition.

Comparison of Vapor and Rigid Glass Spectra

The spectrum of diphenylene in EPA glass at −183° C is shown as a dotted curve on Fig. 1. The whole spectrum was shifted about 370 cm^{-1} to the blue in order to clarify the more important features. The essential dissimilarities between the vapor and rigid glass spectra were as follows:

(1) The 25,780 cm^{-1} lowest-energy vapor band now appears strongly at 3934.9 Å (25,414 cm^{-1}). The one–one correspondence between the bands in the vapor and rigid glass spectra is clearly shown in Table I.

TABLE I

Comparison of the vapor and rigid glass spectra of the weak system of diphenylene

ν_{max} (cm^{-1})		Relative intensity		
Vapor	Glass	Vapor	Glass	$\Delta\nu$ (cm^{-1})
25,407*	25,041	0	0.3	366 (calc.)
25,780	25,414	0.2	1.6	366
26,171	25,833	1.0	1.0	338
26,582	26,195	1.1	1.0	387
26,941	26,578	1.4	2.5	363
27,342	26,928	2.3	5.25	414
27,686	27,320	3.1	2.5	366

*See Table III.

(2) A new band is present at 25,041 cm^{-1} (3993.4 Å). This band is weak in the glass

but does not appear at all in the vapor spectra even at the highest temperatures studied (190° C).

(3) The intensity distribution throughout the band system is quite different to that in the vapor (see Table I). The relative intensities were measured after first subtracting out an estimated contribution from the tail of the higher energy transition.

(4) Each vibrational envelope is shifted to the red of the corresponding vapor band by 366 ± 24 cm^{-1}.

Higher Electronic Transitions

The vapor spectrum of diphenylene at 95° C down to 3000 Å is shown on Fig. 2.

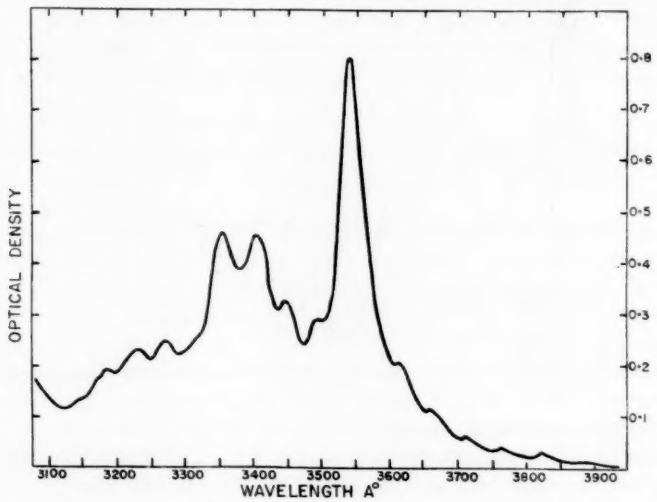

FIG. 2. Vapor spectrum of diphenylene.

Each band in this spectrum correlates with a band in the spectrum of diphenylene in liquid solution.

DISCUSSION

A proposed vibrational analysis of the absorption spectrum is given in Table II. The

TABLE II

Vibrational assignments in the weak system of diphenylene in a rigid EPA glass at 90° K

λ_{max} (Å)	ν_{max} (cm^{-1})	Assignment	$\nu_{obs} - \nu_{calc}$ (cm^{-1})
3993.4	25,041	0–0	0
3934.9	25,414	0+365	+8
3871.2	25,833	0+792	0
3817.6	26,195	b+365	+3
3762.6	26,578	b+2×365	−5
3713.6	26,928	b+3×365	+10
3660.4	27,320	b+4×365	−17

band origin was taken as 25,833 cm^{-1} in the glass and 26,171 cm^{-1} in the vapor. This band starts a long progression of what is almost certainly a symmetric vibration of

frequency 365 cm^{-1} in the upper state. The intensity distribution shows that the nuclear configurations are probably very different in the ground and excited states. The band due to the excitation of three quanta of 365 cm^{-1} is the most intense in the rigid glass. The vibrational interval was about 30 cm^{-1} greater in the spectrum of the vapor. The value of 365 cm^{-1} most probably corresponds to an a_g skeletal mode of diphenylene and may be compared with similar modes in naphthalene (485 cm^{-1} in $^1B_{2u}$) (5) and anthracene (399 cm^{-1} in $^1B_{2u}$) (6) and tetracene (309 cm^{-1} in $^1B_{2u}$) (7).

The 0–0 band of the electronic transition is taken to lie at 25,407 cm^{-1} in the vapor and 25,041 cm^{-1} in the rigid glass. The change in relative intensity of this band between the two media is taken as evidence of a symmetry-forbidden transition. Under these conditions the origin of the totally symmetric sequence was not the 0–0 band but instead was the band at 25,833 cm^{-1}, which is removed by 792 cm^{-1} from the 0–0 band. It is very likely that this interval represents one quantum of an antisymmetric vibration in the upper state. This vibration (represented as b in Table II) makes the electronic transition allowed and thus appears added to each of the other vibrational transitions. If the pure electronic part of the transition was symmetry-forbidden then of course the 0–0 band would not appear at all in the vapor at low pressure. However, in the rigid glass the environmental interactions will probably remove symmetry restrictions to some degree. The same could happen through intramolecular interactions in the vapor at higher pressures or through the excitation of low-lying ground state vibrations at the higher temperatures. The band at 25,414 cm^{-1} (rigid glass) was very weak in the vapor but much stronger in the rigid glass and in liquid solution at room temperature. This band was assigned to an excitation of one totally symmetric vibrational quantum in the upper state. Such a transition is symmetry-forbidden in vibronic symmetry and would either not appear or appear only weakly in the vapor. However, in asymmetric solvent fields a transition of this type might gain considerable intensity over that in the vapor. In other words the intensity of this band is derived from the relaxation of symmetry selection rules due to solvent-induced asymmetry. The lack of detail in the spectra does not permit other than a tentative acceptance of this explanation. The appearance of a vibronic level of this nature could evidence the fact that the molecule has changed its shape during excitation.

To summarize, there were five factors which, when considered together, provided an indication that this lowest electronic transition of diphenylene was forbidden by symmetry and made allowed by the simultaneous excitation of a vibration of the appropriate symmetry. These were as follows:

(1) The extremely low intensity of the electronic absorption. Because of the interference from the higher-energy band it was not possible to obtain an exact value for the f-number of the transition. However, this was estimated to be less than 10^{-3} at liquid nitrogen temperature. This factor alone, although at first sight convincing, was not sufficient evidence of a forbidden transition. The lowest-energy bands in naphthalene and phenanthrene have f-numbers of 2×10^{-3} and 3×10^{-3} (8) respectively and yet are apparently allowed by molecular symmetry. According to the Free Electron Perimeter model (9) these low intensities may be accounted for by the large change in orbital angular momentum associated with these transitions.

(2) The absence of the ascribed 0–0 transition in the vapor phase. Once again this is not a sufficient criterion for symmetry forbiddenness. The 0–0 band of naphthalene is extremely weak or absent in the vapor of naphthalene although it does appear in solution due to the asymmetry field of solvent molecules (2, p. 134). However, the non-appearance

of the 0–0 transition strongly suggests that the electronic transition being studied is forbidden by symmetry.

(3) The marked change in intensity distribution; in particular, the gain in intensity of the 0–0 band in the rigid glass compared to that in the vapor. The over-all intensity distribution and the changes which occur between vapor and rigid glass suggest that Franck–Condon limitations, imposed by a change of symmetry in the upper state, are in operation.

(4) The vibrational analysis, although severely limited by the resolution of the instrument, fully supports the interpretation of a symmetry-forbidden electronic transition. The observed frequencies fit well into the classical series for an electronic transition which is only given intensity by electronic–vibrational coupling in the upper state.

(5) One further piece of evidence which supports our interpretation can be gleaned from the absorption spectrum of diphenylene in solution at room temperature. Figure 3

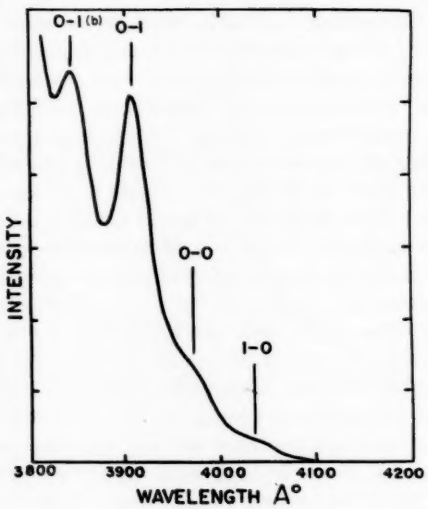

FIG. 3.

shows the absorption spectrum of the long wavelength tail of a highly purified sample of diphenylene in hexane. The two shoulders on the edge are characteristic of the spectra of molecules exhibiting forbidden transitions. In the usual case, when the absorption is to an allowed level, the 0–0 band is very strong. Thus the weak 1–0 band is seldom observed, even as a shoulder, as it is hidden by the strong 0–0 band. In the forbidden case the 0–0 band usually appears very weakly under solvent perturbations and the 1–0 band may then be observed as a shoulder or as a well-defined peak. Thus absorption to a forbidden level would give rise to a strong band (0–1) and then two shoulders corresponding to 0–0 and 1–0 transitions. This is shown quite clearly on Fig. 3. The 1–0 band was naturally not observed in the rigid glass at −183° C because of the Boltzmann factor in the ground state.

Comparison with Theory

The known data for diphenylene is summarized in Table III. The theoretical computations were made by Rowlands (10) using the ASMO–LCAO method. The symmetries were predicted from the table of orbital symmetries of Coulson and Daudel (11).

TABLE III

Comparison of theory and experiment for diphenylene

Theory (9)		Experiment	
0–0 energy (cm^{-1})	Symmetry	0–0 energy (cm^{-1})	Symmetry
17,660	$^1B_{1g}$(forbidden)	25,407*	Forbidden
25,760	$^1B_{2u}$(long axis)	28,200†	$^1B_{2u}$§
39,410	$^1B_{2u}$(long axis)	40,250‡	—

*In the vapor; calculated as 25,041 (glass) − 366 cm^{-1}.
†Vapor ±25 cm^{-1}.
‡Solution at room temperature: see reference 1.
§See reference 3.

On the assumption that diphenylene is a planar molecule (see Fig. 4) belonging to

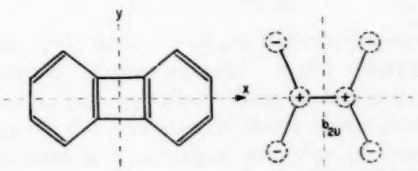

FIG. 4. Diphenylene, $C_{12}H_8$. The axes chosen are those of reference 11. The circles indicate the motion of the nuclei during the execution of a B_{2u} normal vibration within a D_{2h} nuclear framework. The b_{3u} normal vibrations involve asymmetric in-plane motions.

the point group D_{2h} then the lowest excited singlet molecular level is predicted to be $^1B_{1g}$. Transitions from the $^1A_{1g}$ ground state to this level are forbidden by symmetry. They may, however, be made allowed by vibrations of appropriate symmetry which in this case could be b_{2u} or b_{3u}. The symmetry of the resulting vibronic state will be either B_{3u} ($= b_{2u} \times B_{1g}$), which is long axis polarized or B_{2u} ($= b_{3u} \times B_{1g}$), which is short axis polarized. Fundamental vibrations belonging to the representations b_{2u} and b_{3u} should appear in the infrared spectrum of diphenylene.

Our analysis has assumed that the perturbing vibration has frequency 792 cm^{-1}. The infrared spectrum of diphenylene in carbon tetrachloride solution has only two very strong bands in this region. These infrared vibration frequencies are 963 cm^{-1} and 732 cm^{-1}.

The closeness of the 732 cm^{-1} infrared frequency to that of the observed perturbing vibration supports the contention that the electronic transition is of g–g character and made allowed by this b_u vibration. If this deduction is correct then the spectrum should exhibit *two* strong progressions; the first involving the excitation of 1, 2, 3, 4, etc. quanta of an a_g vibration in combination with one b_u quantum; the second involving the successive excitation of 1, 3, 5, etc. quanta of the symmetric b_u vibration. Unfortunately the energy of $0+3b_u$, which is 27,417 cm^{-1}, would place this band right under the strong 27,910 cm^{-1} origin of the next highest electronic state. Such a band could probably not be (and was not) observed in absorption.

The wide discrepancy between the observed and calculated energy of the weak 25,407 cm^{-1} band cannot be explained at the moment. The results of the present experiments do not completely exclude the possibility that this band corresponds to the calculated 25,760 cm^{-1}, $^1B_{3u}$ level.

A detailed examination of the infrared spectrum and of the crystal spectrum should make possible an unambiguous decision as to the nature of the perturbing vibration.

ACKNOWLEDGMENTS

The author would like to thank Dr. J. R. Rowlands both for the sample of diphenylene and some interesting discussions.

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ELECTRODE POTENTIALS OF THE URANIUM CHLORIDES IN FUSED ALKALI CHLORIDE SOLUTIONS[1]

S. N. FLENGAS[2]

ABSTRACT

Using a silver – silver chloride reference electrode, the electrode potentials of the system U, UCl_3(KCl, NaCl) and the redox potentials of the system Pt, UCl_3, UCl_4(KCl, NaCl) were measured at various concentrations of the uranium chlorides and at temperatures between 650 and 850° C.

From the results, the electrode potential of the system U, UCl_4(KCl, NaCl) was calculated. In addition, the activity coefficients and partial molal properties of dilute solutions of UCl_3 and UCl_4 in the equimolar mixture of potassium and sodium chlorides were calculated.

INTRODUCTION

In previous publications (1–7) from the Mines Branch, measurements of the "apparent standard electrode potentials" of several metal – metal chloride systems in dilute solutions in fused alkali chlorides were reported. These measurements were made to provide fundamental information on the activities in fused alkali chloride solutions, to determine the equilibrium constants of chemical reactions in fused salts, and to provide some of the necessary data for studies of the electrolytic reduction of metals from alkali chloride melts.

In determining the electrode potentials, an equimolar mixture of potassium and sodium chlorides was used as the solvent for the metal chlorides, and a silver – silver chloride electrode developed earlier in this work (1) was used as a zero potential reference electrode.

In the experimental work reported here, the technique has been applied to the determination of the potentials of the uranium chlorides dissolved in an equimolar mixture of potassium and sodium chlorides. There are only two stable uranium chlorides at temperatures above 500° C, namely uranium trichloride and uranium tetrachloride. The electrode potentials of the two uranium ions and the redox potentials of the tri- and tetra-valent uranium ions were determined.

EXPERIMENTAL

The cells used for the measurement of the electrode potentials of uranium trichloride, and for the measurement of the redox potentials of the tri- and tetra-valent uranium chlorides, were similar in design to those described in the previous publications (6, 7).

The cell for measuring the electrode potential of uranium trichloride can be represented as follows:

$$\begin{array}{c} U_{(s)} \\ (-) \end{array} \Big| \begin{array}{l} UCl_3\,(x_2) \\ KCl + NaCl\,(1/1\text{ mole}) \end{array} \Big\| \begin{array}{c} \text{Asbestos fiber} \\ \text{diaphragm} \end{array} \Big\| \begin{array}{l} AgCl\,(x_1) \\ KCl + NaCl\,(1/1\text{ mole}) \end{array} \Big| \begin{array}{c} Ag_{(s)} \\ (+) \end{array}$$

The cell reaction is:

$$U_{(s)} + 3Ag^{+}_{(AgCl\text{ in }KCl + NaCl)} = U^{3+}_{(UCl_3\text{ in }KCl + NaCl)} + 3Ag_{(s)}$$

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Contribution from the Extraction Metallurgy Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada. Published with the permission of the Director, Mines Branch.
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The relationship between the electromotive force and the metal ion concentration in the cell is given by the Nernst equation in the form:

$$[1] \quad E_{cell} = (E^\circ_{UCl_3} - E^\circ_{AgCl}) - (2.303RT/3\mathcal{F}) \log(x_2/x_1^3) - (2.303RT/3\mathcal{F}) \log(\gamma_2/\gamma_1^3)$$

where $E^\circ_{UCl_3}$ and E°_{AgCl} are the formation potentials of uranium trichloride and silver chloride in their standard states. The standard state will be defined as the state of the pure metal chloride at the temperature of the experiments.

The γ and x terms are respectively the mean activity coefficients and the conventional mole fractions of the metal chlorides in the solutions in the two half-cells. The activity coefficient of silver chloride in these solutions was determined and found to be unity in a previous investigation (6), using a chlorine electrode.

Following the same method as used previously (6, 7), it is possible, from equation [1], to calculate the "apparent standard cell potential" of the system, by plotting the experimental potential E_{cell} against $\log (x_2/x_1^3)$ and extrapolating the linear relationship to zero log term. The "apparent standard cell potential" obtained in this way is a constant of the system investigated, and is related to the formation potentials of the metal chlorides and the activity coefficient of uranium trichloride by the equation:

$$[2] \quad E^\circ_{app} = (E^\circ_{UCl_3} - E^\circ_{AgCl}) - (2.303RT/3\mathcal{F}) \log \gamma_2.$$

Since the formation potentials of the metal chlorides in their pure state are listed in the literature (8), equation [2] can be used for the determination of the activity coefficient of UCl_3 in the chloride melt.

The cell for measuring the "redox potentials" of the tri- and tetra-valent uranium ions can be represented as follows:

$Pt_{(s)}$ (−)	UCl_3 (x_2) UCl_4 (x_3) KCl + NaCl (1/1 mole)	‖	Asbestos fiber diaphragm	‖ AgCl (x_1) KCl + NaCl (1/1 mole)	$Ag_{(s)}$ (+)

The cell reaction is:

$$U^{3+}_{(UCl_3 \text{ in KCl + NaCl})} + Ag^+_{(AgCl \text{ in KCl + NaCl})} = U^{4+}_{(UCl_4 \text{ in KCl + NaCl})} + Ag_{(s)}.$$

The relationship between the cell potential and the metal ion concentration in the cell is given by the Nernst equation in the form:

$$[3] \quad E_{cell} = (E^\circ_{UCl_3/UCl_4} - E^\circ_{AgCl}) - (2.303RT/\mathcal{F}) \log (x_3/x_1 . x_2) - (2.303RT/\mathcal{F}) \log (\gamma_3/\gamma_1 . \gamma_2)$$

where the $E^\circ_{UCl_3/UCl_4}$ is the standard redox potential of the system UCl_3, UCl_4 in the standard state. The x and γ terms are, respectively, the mole fractions and the activity coefficients of the metal chlorides.

The "apparent standard redox" potential of the system is determined by plotting the experimental cell potentials against $\log (x_3/x_1 . x_2)$ and then extrapolating the linear relationship to zero log term.

It should be noted that the above-mentioned cells were operated in an inert atmosphere of purified argon gas.

PREPARATION OF MATERIALS

The equimolar mixture of potassium and sodium chlorides was prepared from analytical grade reagents, and was dehydrated by heating under vacuum at 500° C for 12 hours.

Anhydrous uranium trichloride was prepared in a tubular furnace at 500° C, by the reaction between reactor grade uranium metal and oxygen-free anhydrous hydrogen

chloride (9). Very pure and dry gaseous hydrogen chloride was prepared in a suitable apparatus by the reaction between concentrated hydrochloric acid and concentrated sulphuric acid (10). The product of the reaction, between uranium metal and hydrogen chloride, was finely divided uranium trichloride which adhered to the surface of the metal. This finely powdered product, which was separated from the coarse unreacted uranium by sieving in a dry box, was of a purity of 98.5%.

Anhydrous uranium tetrachloride was prepared by the reaction between hydrated uranium trioxide ($UO_3.2H_2O$) and hexachloropropene (11). The product obtained from this reaction was purified by sublimation *in vacuo*, and was of a purity of 99.0%.

The uranium chlorides were pelletized in an argon-filled dry box and were transferred to the cell using the piston-type feeding apparatus described previously (7).

The uranium electrode for these experiments was a rod of reactor grade uranium which had been swaged down to $\frac{1}{2}$-in. diameter, and was about 3 in. long. It was connected to a platinum wire. Prior to its use, the electrode was polished to a silver-like finish in a dilute solution of nitric acid. The polished electrode was then washed with distilled water and dried with acetone.

The silver electrode was a rod of pure silver (99.9%) connected to a silver wire. The inert platinum electrode used for the redox potential measurements was a hollow platinum cylinder of $\frac{1}{2}$-in. diameter and 3-in. long. It was connected to a platinum wire.

The thermoelectric potentials due to the bimetallic systems of these electrodes were measured separately, and the appropriate corrections were applied to the measurements of the electrode potentials.

RESULTS

1. Electrode Potentials of the U/U^{3+} System

In the preliminary experiments, the stability of a system consisting of uranium metal immersed in a solution of uranium trichloride in molten potassium and sodium chlorides was investigated by following the change of the cell potential with time.

The solutions of uranium trichloride were prepared *in situ* during the run, by adding weighed pellets of the anhydrous salt to the melt in the indicator electrode compartment. After each addition, the equilibrium potential was attained in about 30 minutes. Potential readings were then taken at regular time intervals over a period of about 20 hours. It was found that the shift of potential was of the order of only 1 mv. Furthermore, after the end of the run there was no indication of a chemical attack on the uranium electrode.

It was concluded that uranium metal is insoluble in dilute solutions of uranium trichloride under the conditions of the experiment. However, it was observed that electrodes which accidentally had been placed in contact with the side walls of the silica tubing in the cell were heavily corroded. The potentials obtained under these conditions were erratic and non-reproducible. In all probability, the observed solubility of uranium metal in the melt was due to the formation of a soluble uranium oxide or oxychloride through the exchange reaction between uranium metal and silica. For this reason, during the experiments, the uranium electrode was suspended by the platinum wire in the center of the cell.

The electromotive force of the U/U^{3+} cell was measured first as a function of temperature, at various mole fractions of uranium trichloride.

The variation of the cell potential with temperature, at mole fractions varying between 10^{-4} and 10^{-2}, is shown in Fig. 1. The results in this graph represent three independent runs. It is apparent that the curves are linear over the temperature range between 650

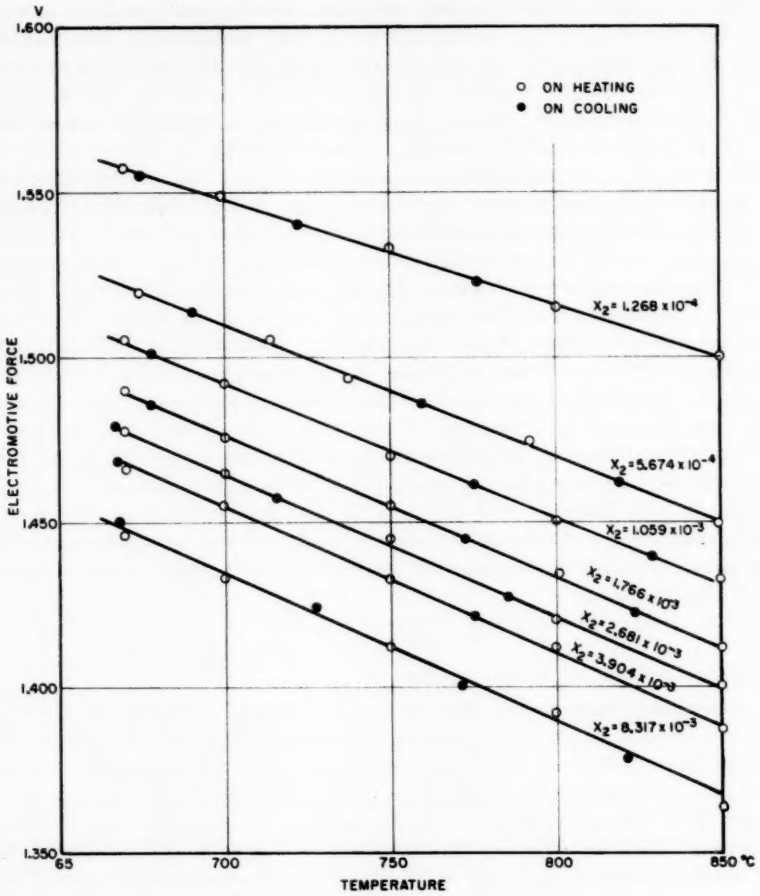

FIG. 1. Electromotive force of the cell:

$$\begin{array}{c|c|c|c|c} \text{U} & \text{UCl}_3\ (x_2) & \| & \text{AgCl}\ (x_1 = 5.0\times10^{-2}) & \text{Ag} \\ (-) & \text{KCl} + \text{NaCl}\ (1/1\ \text{mole}) & \| & \text{KCl} + \text{NaCl}\ (1/1\ \text{mole}) & (+) \end{array}$$

as a function of temperature.

and 850° C, and the cell potentials have a negative temperature coefficient. Potential readings made while temperature was being increased were in good agreement with those made while the temperature was decreasing.

The relationship between the cell potential and the logarithm of the mole fractions, at temperatures between 670 and 850° C, is shown in Fig. 2. In this graph the straight lines through the experimental points are the best straight lines that can be drawn with a slope equal to the slope of the Nernst equation for a three-electron electrode reaction at these temperatures. It is seen that the results are in agreement with the Nernst equation. The linearity of the curves indicates that the activity coefficient of uranium trichloride in these dilute solutions is independent of concentration. The "apparent standard cell potential" of uranium trichloride was obtained by extrapolation of the curves to zero log (x_2/x_1^3) term. These results are given in Table I.

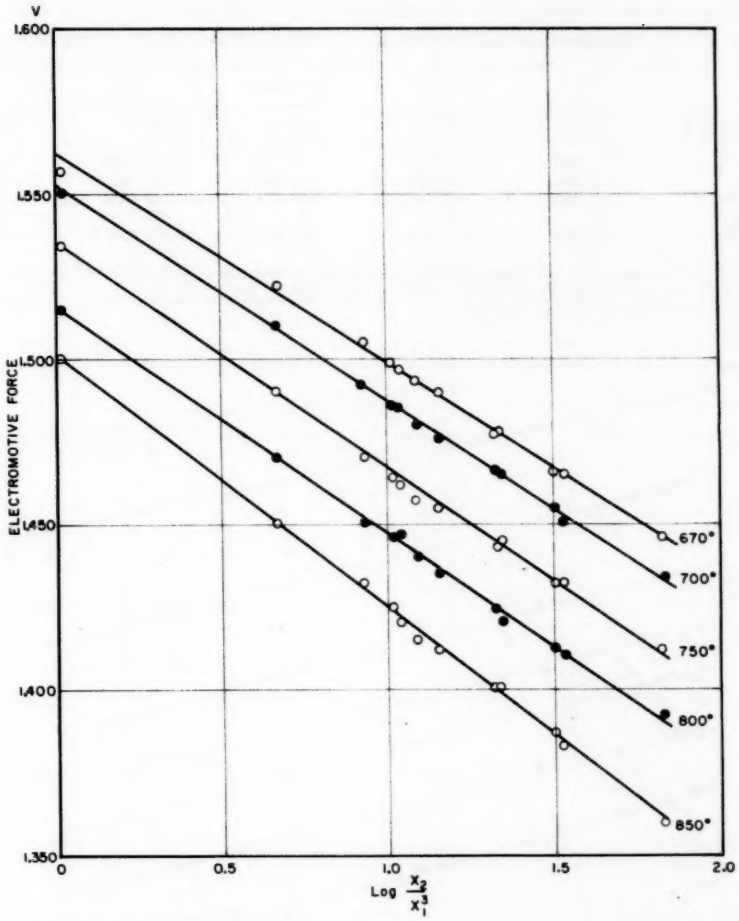

FIG. 2. Electromotive force of the cell:

$$\begin{array}{c|c|c|c|c} \text{U} & \text{UCl}_3\ (x_2) & \text{AgCl}\ (x_1 = 5.0\times10^{-2}) & \text{Ag} \\ (-) & \text{KCl} + \text{NaCl}\ (1/1\ \text{mole}) & \text{KCl} + \text{NaCl}\ (1/1\ \text{mole}) & (+) \end{array}$$

as a function of log (x_2/x_1^3), at various temperatures.

2. "Redox" Potentials of the U^{3+}/U^{4+} System

The electromotive force of the U^{3+}/U^{4+} redox cell was measured, as a function of temperature, at various mole fractions of uranium tri- and tetra-chlorides. The stability of the potential measurements over a period of time exceeding 12 hours indicated that solutions of uranium tri- and tetra-chlorides in the equimolar mixture of potassium and sodium chlorides are very stable.

The results of the redox potential measurements at temperatures between 650 and 850° C, for mole fractions of uranium tri- and tetra-chlorides varying between 10^{-3} and 10^{-2}, are shown in Fig. 3.

It is seen that the curves are linear over the temperature range investigated, and that the potentials of the redox cells have a negative temperature coefficient.

TABLE I

Apparent standard potentials in 1/1 mole KCl + NaCl

Indicator electrode	E_0' (volts)*				
	670° C	700° C	750° C	800° C	850° C
U, U^{3+}	−1.563	−1.554	−1.535	−1.519	−1.502
U, U^{4+}	−1.295	−1.285	−1.269	−1.252	−1.239
U^{3+}, U^{4+}	−0.494	−0.483	−0.473	−0.459	−0.450
Ag, Ag^+	0	0	0	0	0
Cl^-, Cl†	+0.852	+0.845	+0.832	+0.820	+0.807

*It will be noted that the sign of the experimentally obtained apparent standard potentials shown in this table has been altered to conform with the recommendations of the IUPAC Stockholm convention, as reported by Light and deBethune (12).

†The potential of the chlorine electrode against the silver – silver (6) chloride electrode was determined in a previous investigation, and the results are shown here for comparison.

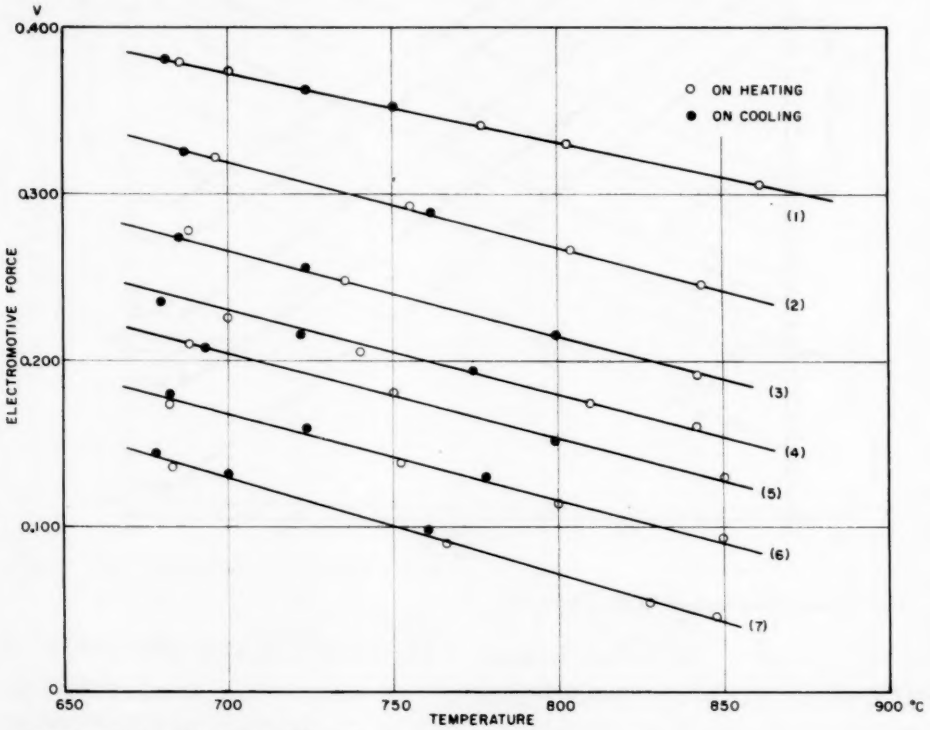

FIG. 3. Electromotive force of the cell:

Pt	UCl_3 (x_2)	‖	AgCl ($x_1 = 5.0\times10^{-2}$)	Ag
(−)	UCl_4 (x_3)		KCl + NaCl (1/1 mole)	(+)
	KCl + NaCl (1/1 mole)			

as a function of temperature at mole fractions:

(1) $x_2 = 8.303\times10^{-3}$, $x_3 = 1.703\times10^{-3}$

(2) $x_2 = 8.287\times10^{-3}$, $x_3 = 3.527\times10^{-3}$

(3) $x_2 = 8.232\times10^{-3}$, $x_3 = 6.254\times10^{-3}$

(4) $x_2 = 2.445\times10^{-3}$, $x_3 = 2.671\times10^{-3}$

(5) $x_2 = 5.697\times10^{-3}$, $x_3 = 9.601\times10^{-3}$

(6) $x_2 = 2.447\times10^{-3}$, $x_3 = 5.723\times10^{-3}$

(7) $x_2 = 2.438\times10^{-3}$, $x_3 = 9.629\times10^{-3}$

The relationship between the cell potential and the logarithm of the mole fractions, at temperatures between 670 and 850° C, is shown in Fig. 4. In this graph the straight

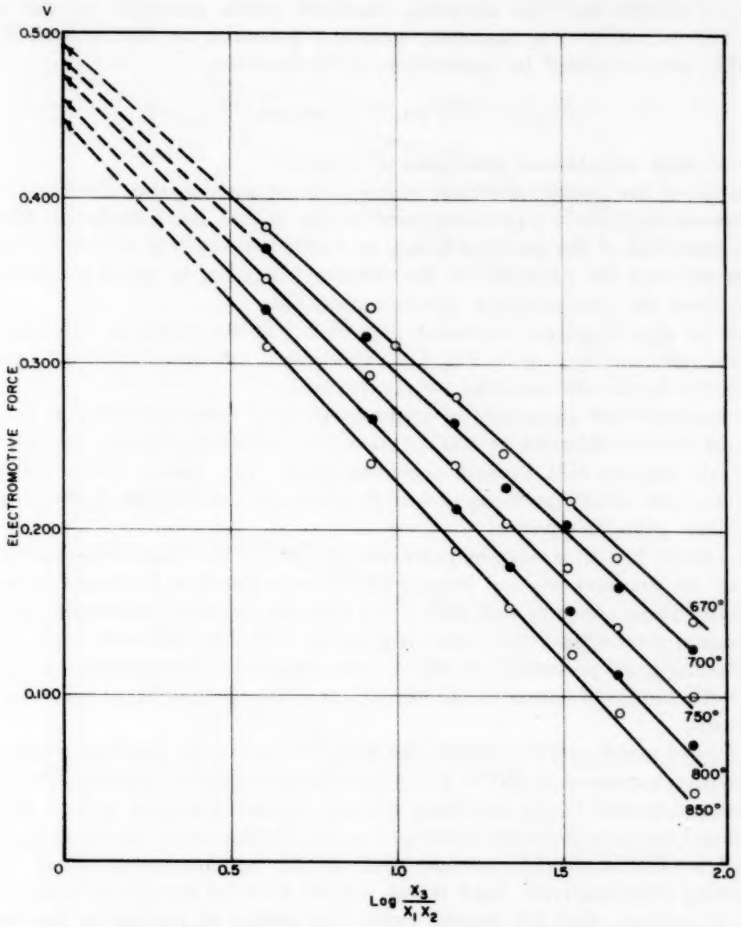

FIG. 4. Electromotive force of the cell:

Pt	UCl_3 (x_2)	‖	AgCl ($x_1 = 5.0\times10^{-2}$)	Ag
(−)	UCl_4 (x_3)		KCl + NaCl (1/1 mole)	(+)
	KCl + NaCl (1/1 mole)			

as a function of $\log (x_3/x_1.x_2)$, at various temperatures.

lines through the experimental points are the best straight lines that can be drawn with a slope equal to the slope of the Nernst equation for a one-electron electrode reaction at these temperatures. It is seen that the results agree well with the Nernst equation. The linearity of these curves indicates that the activity coefficient of uranium tetrachloride in these dilute solutions is independent of concentration.

The "apparent standard redox potential" of the system was obtained by extrapolation of the curve to zero $\log (x_3/x_2.x_1)$. These results are given in Table I.

DISCUSSION

From the experimental values for the apparent standard potentials of the system $U/UCl_3(KCl + NaCl)$ and the apparent standard redox potential of the system $UCl_3/UCl_4(KCl + NaCl)$, the apparent standard potential of the system U/UCl_4 $(KCl + NaCl)$ was calculated by application of the equation:

$$[4] \qquad E^\circ_{UCl_4} = (3E^\circ_{UCl_3} + E^\circ_{UCl_3/UCl_4})/4.$$

The results of these calculations are shown in Table I.

The potentials of the chlorine electrode which were measured against the silver – silver chloride reference electrode in a previous investigation (6) are also included in this table. To refer the potentials of the uranium system to a chlorine reference electrode, it is only necessary to subtract the potential of the chlorine electrode, as given at the bottom of the table, from the corresponding uranium potential.

The graph of the "apparent standard potentials" of the uranium chlorides, as a function of temperature, is given in Fig. 5. In this graph, calculated standard potentials of the pure salts (8) are also included for comparison.

Apparent standard cell potentials of uranium tri- and tetra-chlorides, in a melt of potassium and lithium chlorides at 450° C, have been reported recently by Gruen and Osteryoung (13), and by Hill, Ferand, and Osteryoung (14). Inman, Hills, Young, and Bockris (15, 16) also investigated the potentials of uranium trichloride in the potassium chloride – lithium chloride eutectic.

When the results in Fig. 5 were extrapolated to 450° C, the "apparent standard cell potentials" of the uranium tri- and tetra-chlorides were found to be respectively 1.632 and 1.365 volts. These compare well with 1.611 volts for uranium trichloride, and 1.363 volts for uranium tetrachloride given by Gruen *et al.* (13), and Hill *et al.* (14). Also the "apparent standard cell potential" at 450° C, of uranium trichloride which can be calculated from the results of Inman *et al.* (15, 16), is of the same order of magnitude, i.e. about 1.66 volts.

For a variety of metal – metal chloride systems, the agreement between the apparent standard potential measured at 450° C in the eutectic of potassium and lithium chlorides (17), and those measured in the equimolar mixture of potassium and sodium chlorides, has been pointed out in a previous investigation (6). Furthermore, the same agreement was observed by Hill *et al.* (14) in their study of the uranium potentials in chloride melts containing comparatively light metal cations such as potassium, lithium, and magnesium. It appears that the partial molal free energy of mixing of the uranium chlorides is almost independent of the size of the cations present in the solvent, provided that these cations are much smaller than the uranium ions.

From the apparent standard potentials shown in Table I, it is possible to calculate the thermodynamic functions and the equilibrium constants of various reactions of metallurgical interest. The results of these calculations are given in Table II.

The magnitude of the equilibrium constant for reaction [4], shown in Table II, indicates that in the presence of uranium metal, uranium tetrachloride would be reduced quantitatively to the trichloride.

The equilibrium constants of reactions [1] to [3] indicate that uranium metal will displace silver ions from solution, and that at equilibrium, the predominant species will be uranium tetrachloride.

Using the results in Fig. 5, the partial molal properties and the activity coefficients

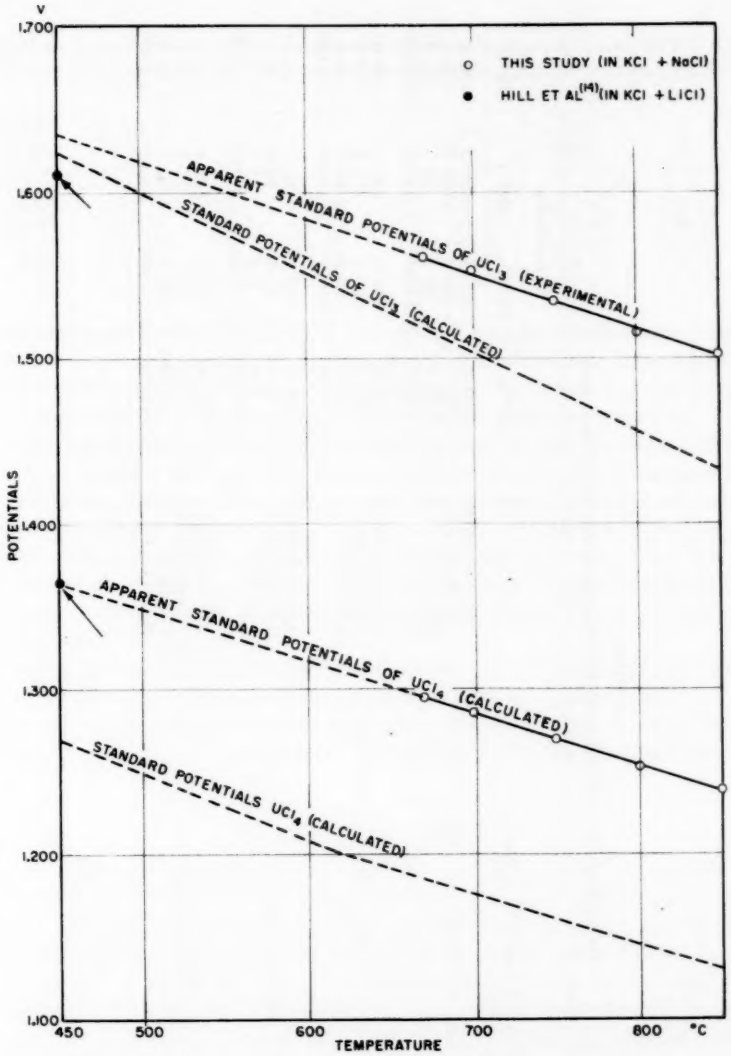

FIG. 5. Apparent standard potentials of UCl_3 and UCl_4 and the corresponding standard state potentials at various temperatures.

of the uranium chloride solutions were calculated from the differences between the "standard potentials" of the pure uranium tri- and tetra-chlorides and the "apparent standard potentials" in the fused salt solution. The results of these calculations are given in Table III.

The partial molal free energy of solution ($\Delta\bar{F}$), given in Table III, represents the difference between the free energy of the salt in its hypothetical standard state as a solute, i.e., "a solution containing a unit mole fraction of the salt but having in all other

TABLE II

Thermodynamic calculations for reactions involving the uranium ions

Reaction in 1/1 mole KCl + NaCl		Temperature 670° C	750° C	800° C	850° C
(1) $U_{(s)} + 3Ag^{+}_{(AgCl \text{ in } KCl + NaCl)} = U^{3+}_{(UCl_3 \text{ in } KCl + NaCl)} + 3Ag_{(s)}$	ΔH (kcal/mole)	−130.2	−130.2	−130.2	−130.2
	ΔF (kcal/mole)	−108.1	−106.2	−105.1	−103.9
	ΔS (e.u.)	− 23.4	− 23.4	− 23.4	− 23.4
	K	1.1×10^{25}	4.8×10^{22}	2.5×10^{21}	1.6×10^{20}
(2) $U_{(s)} + 4Ag^{+}_{(AgCl \text{ in } KCl + NaCl)} = U^{4+}_{(UCl_4 \text{ in } KCl + NaCl)} + 4Ag_{(s)}$	ΔH (kcal/mole)	−136.0	−136.0	−136.0	−136.0
	ΔF (kcal/mole)	−119.4	−117.0	−115.5	−114.3
	ΔS (e.u.)	− 17.6	− 18.5	− 19.1	− 19.3
	K	4.7×10^{27}	1.0×10^{25}	3.3×10^{23}	1.7×10^{22}
(3) $U^{3+}_{(UCl_3 \text{ in } KCl + NaCl)} + Ag^{+}_{(AgCl \text{ in } KCl + NaCl)} = U^{4+}_{(UCl_4 \text{ in } KCl + NaCl)} + Ag_{(s)}$	ΔH (kcal/mole)	− 16.7	− 16.7	− 16.7	− 16.7
	ΔF (kcal/mole)	− 11.4	− 10.9	− 10.9	− 10.4
	ΔS (e.u.)	− 5.6	− 5.6	− 5.6	− 5.6
	K	4.3×10^{2}	3.3×10^{2}	1.4×10^{2}	1.0×10^{2}
(4) $3U^{4+}_{(UCl_4 \text{ in } KCl + NaCl)} + U_{(s)} = 4U^{3+}_{(UCl_3 \text{ in } KCl + NaCl)}$	ΔH (kcal/mole)	−112.8	−112.8	−112.8	−112.8
	ΔF (kcal/mole)	− 74.2	− 73.8	− 73.9	− 72.7
	ΔS (e.u.)	− 40.8	− 38.1	− 36.3	− 35.7
	K	1.5×10^{17}	5.4×10^{15}	1.1×10^{15}	1.4×10^{14}

TABLE III

Partial molal properties of dilute solutions of uranium chlorides in 1/1 mole KCl + NaCl

	UCl_3 in KCl + NaCl				UCl_4 in KCl + NaCl			
t (°C)	$\Delta\bar{F}$ (kcal/mole)	$\Delta\bar{H}$ (kcal/mole)	$\Delta\bar{S}$ (e.u.)	$\gamma\times10^4$	$\Delta\bar{F}$ (kcal/mole)	$\Delta\bar{H}$ (kcal/mole)	$\Delta\bar{S}$ (e.u.)	$\gamma\times10^2$
670	−2.97	+6.170	+9.7	2.05	−10.15	+10.60	+22.0	4.46
750	−3.80	+6.170	+9.7	1.54	−10.05	+10.60	+20.1	7.14
800	−4.50	+6.170	+9.7	1.21	−10.05	+10.60	+19.2	8.97
850	−4.70	+6.170	+9.7	1.22	−10.05	+10.60	+18.4	11.1

respects the thermodynamic properties of the state of infinite attenuation of the solute", as defined by Lewis and Randall (18), and the free energy of the salt in its actual standard state of the pure salt. It is of interest to note that the partial molar free energy of solution of uranium tetrachloride is much greater than that of uranium trichloride.

The activity coefficients and the partial molal entropies of mixing indicate that uranium trichloride and uranium tetrachloride form complexes in solution. A comparison of the activity coefficients indicates that the uranium tetrachloride complex is stronger than the uranium trichloride complex. The variation of the activity coefficients of uranium tetrachloride with temperature shows the expected behavior; i.e., they increase with temperature. On the contrary, the activity coefficients of uranium trichloride decrease with increasing temperature, which indicates that the complexity of uranium trichloride is greater at higher temperatures.

The presence of complexes of tetravalent uranium ions in chloride melts has also been observed by Gruen and McBeth from spectrophotometric studies (19).

The constancy of the activity coefficients over the mole fraction range 10^{-4} to 10^{-2} indicates that the solutions of uranium tri- and tetra-chlorides in fused salts obey Henry's law.

ACCURACY OF RESULTS

It is rather difficult to evaluate the absolute accuracy of the potentials shown in Table I. Individual potential measurements shown in Figs. 1 and 3 were stable and reproducible. The slight scattering of the experimental points, which can be seen in the figures, is probably due to other side effects which are always present in high-temperature systems. These effects are: concentration gradients due to thermal convection currents; difficulties in obtaining a completely oxygen-free uranium metal surface; and slight impurities in the electrolyte. However, judging from the results presented in Figs. 1 to 4, it is reasonable to assume that the potential values obtained in this investigation are accurate to within ±2 mv. This variation would also affect the calculation of the free energy listed in Tables II and III. It has been estimated that the variation of the free energy change should be about ±0.3 kcal/mole for the uranium trichloride system, and about ±0.4 kcal/mole for the uranium tetrachloride system.

ACKNOWLEDGMENTS

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CARBOXYMETHYLMERCAPTO AND CARBOXYMETHYLSULPHONYL DERIVATIVES OF NITROIMIDAZOLE[1]

M. H. FISHER, W. H. NICHOLSON, AND R. S. STUART

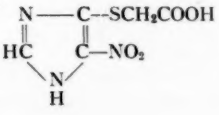
ABSTRACT

Several carboxymethylmercapto and carboxymethylsulphonyl derivatives of nitroimidazole were prepared for biological testing. Reduction or reductive cyclization of these compounds was unsuccessful.

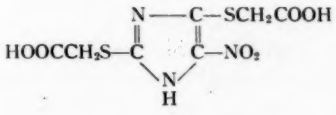
INTRODUCTION

In a previous communication (1) the syntheses of a number of nitro- and amino-imidazolesulphonamides as potential antimetabolites were described. This work has now been extended to the related carboxymethylmercapto compounds and oxidized derivatives. It was hoped that the nitro compounds could be reduced and cyclized but all attempts led to the formation of colored reaction mixtures from which no pure compounds could be isolated.

4(5)-Bromo-5(4)-nitroimidazole (2), 2,4(5)-dibromo-5(4)-nitroimidazole (2), 4-chloro-1-methyl-5-nitroimidazole (3), and 5-chloro-1-methyl-4-nitroimidazole (3) on treatment with thioglycolic acid in ammoniacal solution gave the carboxymethylmercapto compounds (I), (II), (III), and (IV).



(I)



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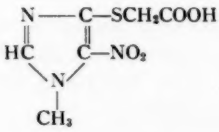

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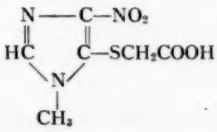
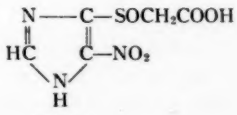


(IV)

Oxidation with hydrogen peroxide in glacial acetic acid yielded the sulphones (V), (VI), and (VII). The disulphide (II) gave an oil which could not be crystallized. The non-methylated compound (I) was somewhat more resistant to oxidation than the others. An intermediate sulphoxide (VIII) was isolated and further oxidized to the sulphone under more vigorous conditions.



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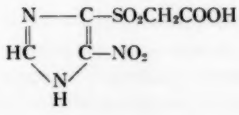

(V)

[1]*Manuscript received December 27, 1960.*
Contribution from the Research Department, Merck & Co. Ltd., Montreal, Que.

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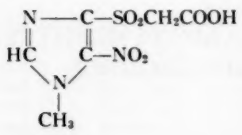

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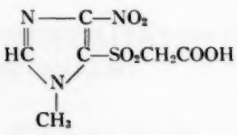
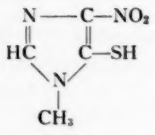


(VII)

Treatment of the sulphide (IV) or the sulphone (VII) with bromine yielded mixtures containing some brominated material. Either mixture with hydrogen sulphide in ammoniacal solution gave 5-mercapto-1-methyl-4-nitroimidazole (IX) (4) as the major product.



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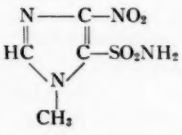

(X)

It was subsequently found that hydrogen sulphide readily displaced the carboxymethylmercapto, the carboxymethylsulphonyl, or the sulphonamide groups from compounds (IV), (VII), or (X). In each case the thiol (IX) was produced in good yield.

EXPERIMENTAL

Carboxymethylmercapto Compounds

2,4(5)-Bis-(carboxymethylmercapto)-5(4)-nitroimidazole (II)

Thioglycolic acid (11 ml) was added to a solution of 2,4(5)-dibromo-5(4)-nitroimidazole (20 g) in water (100 ml) and concentrated ammonia (50 ml). The mixture was allowed to stand at room temperature for 64 hours. Addition of isopropyl alcohol (300 ml) precipitated the yellow ammonium salt (12 g), m.p. 136°.

The ammonium salt was converted to the free acid with Amberlite resin IR-120(H^+). Crystallization from water gave yellow needles, m.p. 212–213°. Found: C, 28.5; H, 2.38; N, 14.1; S, 21.9. Calc. for $C_7H_7N_3O_6S_2$: C, 28.6; H, 2.39; N, 14.3; S, 21.8%.

4-Carboxymethylmercapto-1-methyl-5-nitroimidazole (III)

Thioglycolic acid (7.5 ml) was added dropwise with stirring to a suspension of 4-chloro-1-methyl-5-nitroimidazole (15 g) in water (100 ml) and concentrated ammonia (50 ml). After storage at 5° for 16 hours the ammonium salt was collected as yellow needles (18.5 g), m.p. 185°.

The ammonium salt was converted to the free acid by precipitation from water with hydrochloric acid. Crystallization from ethanol gave pale yellow needles, m.p. 163–164°. Found: C, 33.2; H, 3.26; N, 18.6; S, 14.7. Calc. for $C_6H_7N_3O_4S$: C, 33.2; H, 3.22; N, 19.3; S, 14.7%.

5-Carboxymethylmercapto-1-methyl-4-nitroimidazole (IV)

This compound was prepared from 5-chloro-1-methyl-4-nitroimidazole (15 g) in a similar manner. Addition of isopropanol (300 ml) and ether (150 ml) and storage for 18 hours at 5° precipitated the ammonium salt (16.5 g), m.p. 153–154°. The free acid crystallized from ethanol as jagged white lathes (8.5 g), m.p. 209–210°. Found: C, 33.5; H, 3.25; N, 19.3; S, 14.5. Calc. for $C_6H_7N_3O_4S$: C, 33.2; H, 3.22; N, 19.3; S, 14.7%.

4(5)-Carboxymethylmercapto-5(4)-nitroimidazole (I)

This compound was prepared from 4(5)-bromo-5(4)-nitroimidazole (9 g) in a similar manner. The ammonium salt (9.2 g) was collected after 1 hour. After crystallization from methanol it had a melting point of 193–194°. The free acid crystallized from water as yellow needles (6.7 g), m.p. 185–186°. Found: C, 29.6; H, 2.41; N, 20.4; S, 15.7. Calc. for $C_5H_5N_3O_4S$: C, 29.6; H, 2.48; N, 20.6; S, 15.8%.

Oxidations with Hydrogen Peroxide

4(5)-Carboxymethylsulphoxy-5(4)-nitroimidazole (VIII)

4(5)-Carboxymethylmercapto-5(4)-nitromidazole (2 g) in glacial acetic acid (10 ml) and 30% hydrogen peroxide (10 ml) was heated for 1 hour at 75°. The solution was cooled and the product crystallized as white needles (1.6 g), m.p. 219–220° (decomp.). Recrystallization from water raised the m.p. to 220–221° (decomp.). Found: C, 27.3; H, 2.26; N, 18.8; S, 14.8. Calc. for $C_5H_5N_3O_5S$: C, 27.4; H, 2.28; N, 19.2; S, 14.6%.

4(5)-Carboxymethylsulphonyl-5(4)-nitroimidazole (V)

The sulphoxide (VIII) (1 g) in glacial acetic acid (5 ml) and 30% hydrogen peroxide (5 ml) was heated for 4 hours at 90° until a clear solution was obtained. Evaporation to dryness yielded the product (0.8 g), m.p. 284–286°. Recrystallization from water gave white needles, m.p. 295–296°. Found: C, 25.0; H, 2.20; N, 18.0; S, 13.8. Calc. for $C_5H_5N_3O_6S$: C, 25.5; H, 2.12; N, 17.9; S, 13.6%.

4-Carboxymethylsulphonyl-1-methyl-5-nitroimidazole (VI)

Similar oxidation of 4-carboxymethylmercapto-1-methyl-5-nitroimidazole (5 g) for 1 hour at 85° yielded the product (4 g), m.p. 181–182° (decomp.) as white needles from water. Found: C, 28.9; H, 2.83; N,16.5; S, 13.0. Calc. for $C_6H_7N_3O_6S$: C, 28.9; H, 2.81; N, 16.8; S, 12.8%.

5-Carboxymethylsulphonyl-1-methyl-4-nitroimidazole (VII)

Similar oxidation of 5-carboxymethylmercapto-1-methyl-4-nitroimidazole (2 g) for 1 hour at 80° yielded the product (1.25 g), m.p. 170–171° (decomp.) as white needles from water. Found: C, 29.1; H, 2.81; N, 16.8; S, 13.0. Calc. for $C_6H_7N_3O_6S$: C, 28.9; H, 2.81; N, 16.8; S, 12.8%.

Brominations

5-Carboxymethylmercapto-1-methyl-4-nitroimidazole (0.01 mole) or 5-carboxymethylsulphonyl-1-methyl-4-nitroimidazole (0.01 mole) in 1 *N* sodium hydroxide (10 ml) was treated with bromine (0.012 mole). In both cases the precipitated product was a difficultly separable mixture of partially brominated materials.

Displacements with Hydrogen Sulphide

The partially brominated mixtures, 5-carboxymethylmercapto-1-methyl-4-nitroimidazole, 5-carboxymethylsulphonyl-1-methyl-4-nitroimidazole, or 1-methyl-4-nitro-5-sulphamylimidazole (1) were each dissolved in 5 *N* ammonia (1 g in 10 ml) and hydrogen sulphide passed through for 10 minutes. In each case the product was the ammonium salt of 5-mercapto-1-methyl-4-nitroimidazole.

Reductions

Each of the nitroimidazoles was reduced either with hydrogen and Adams platinum catalyst in ethanol or glacial acetic acid or with powdered zinc and glacial acetic acid. In all cases the solutions became highly colored and only dark brown tars could be isolated.

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COUPLING CONSTANTS IN RIGID FIVE-MEMBERED RINGS

N.M.R. SPECTRA OF THE CAMPHANE-2,3-DIOLS[1]

F. A. L. ANET

ABSTRACT

The proton nuclear magnetic resonance (N.M.R.) spectra of the four diastereoisomers of camphane-2,3-diol are reported. The coupling constants between the 2-, 3-, and 4-protons agree with the values predicted by Karplus for ethane derivatives. In particular, the cis (0° dihedral angle) coupling constants (7.7 and 8.9 c.p.s.) are much larger than the trans (120° dihedral angle) coupling constants (2.2 and 2.3 c.p.s.). Unexpected 1,3-coupling between *exo*-hydrogen atoms occurs in some of the compounds studied.

INTRODUCTION

Indirect spin–spin coupling constants in substituted ethane derivatives have attracted attention because of the dependence of their values on the dihedral angle between the CH bonds involved (1–7). The dihedral angles are 60° and 180° in non-cyclic substituted ethanes, which, in general, exist in staggered rather than eclipsed forms. These are also the dihedral angles between vicinal CH bonds in six-membered rings existing in chair conformations. In each case the observed coupling constants may be weighted averages if more than one conformation exists to an appreciable extent.

Karplus (8) has used a semiempirical method to calculate the coupling constants with variation of the dihedral angle in the system CH–CH. The values for angles from 0° to 180° are plotted (cf. ref. 7) in Fig. 1. Most of the experimental evidence, as already mentioned, relates to the values of coupling constants for angles of 60° and 180°. Although

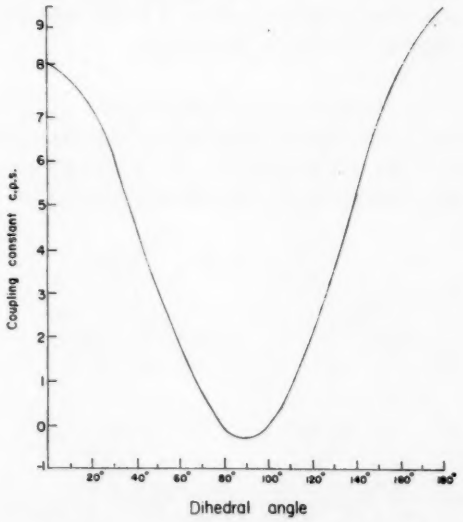

FIG. 1. Variation of coupling constants with dihedral angle in ethane derivatives, as calculated by Karplus (8).

[1]*Manuscript received November 29, 1960.*
Contribution from the Department of Chemistry, University of Ottawa, Ottawa, Canada.

the calculated values for these angles are in satisfactory agreement with the experimental values, it would be highly desirable to determine coupling constants for a whole series of angles from 0° to 180°. The results have a bearing not only in the N.M.R. field (9), but also in other problems, such as that of the origin of the energy barrier in ethane derivatives (10).

There are a few cases in the literature where zero coupling constants have been observed in the case of dihedral angles of about 90°, and these will be referred to at the end of this paper. No case seems to have been reported, however, for 0° or for very small angles. The spectra discussed in this paper provide data for determining coupling constants of the type required for angles of about 0°, 44°, 79°, and 120°.

Owing to the kindness of Dr. S. J. Angyal in providing samples, it has been possible to examine the N.M.R. spectra of the four diastereoisomers of camphane-2,3-diol (11, 12), which are ideal compounds for the present purpose because of the rigid structures of these molecules.

EXPERIMENTAL

The spectra were taken at a frequency of 60 Mc/sec on a Varian V-4302 high-resolution spectrometer. Solutions (10–15%) in pyridine containing a small amount of deuterium oxide and tetramethylsilane were used. Calibration of the spectra was carried out by the usual side-band method. Pyridine solutions were used because the trans isomers were only sparingly soluble in carbon tetrachloride or chloroform. The addition of a small amount of deuterium oxide had the effect of removing the coupling between the OH groups and the adjacent CH groups, thus simplifying the spectra. The OH peak, which had been broad before the addition of deuterium oxide, became quite sharp after the addition. As the OH groups should be strongly hydrogen-bonded with the nitrogen atoms of the pyridine molecules, their occurrence at lower field (ca. 4.6 τ) (5) than the other protons of the camphane diols is not surprising.

RESULTS AND DISCUSSION

The spectra (with the exception of the OH peaks) of the four diols (Fig. 2) are shown in Fig. 3. Slower sweeps of the bands of the 2- and 3-protons are shown in Fig. 4.

In each isomer there are appreciable chemical shifts between the three methyl groups

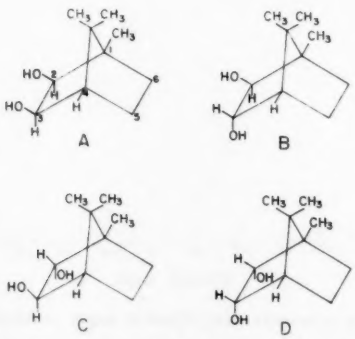

FIG. 2. Stereochemistry of the four camphane-2,3-diols. The diastereoisomers studied were optically active and of the same absolute configuration as (+) camphor (11). A, 2-*exo*,3-*exo*-isomer. B, 2-*exo*,3-*endo*-isomer. C, 2-*endo*,3-*exo*-isomer. D, 2-*endo*,3-*endo*-isomer.

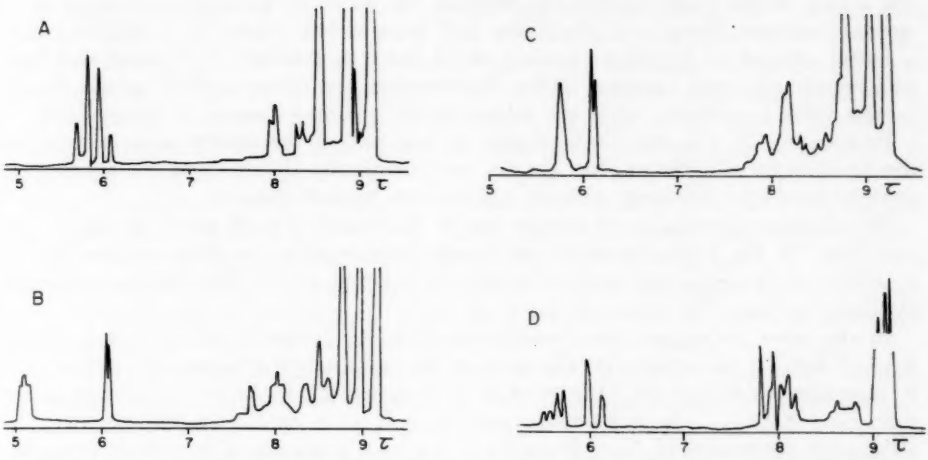

FIG. 3. N.M.R. spectra of the camphane-2,3-diols. A, 2-*exo*,3-*exo*-isomer. B, 2-*exo*,3-*endo*-isomer. C, 2-*endo*,3-*exo*-isomer. D, 2-*endo*,3-*endo*-isomer.

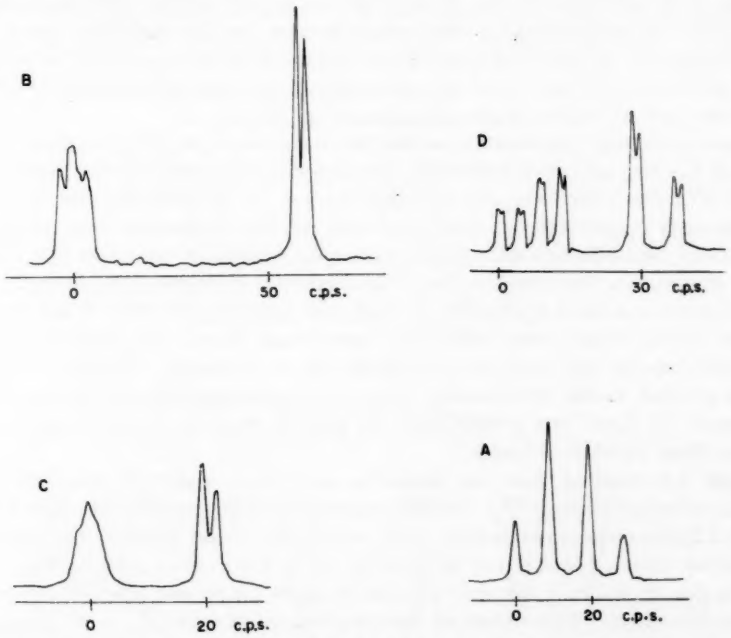

FIG. 4. Slow sweep of the 2- and 3-protons of the camphane-2,3-diols. A, 2-*exo*,3-*exo*-isomer. B, 2-*exo*,3-*endo*-isomer. C, 2-*endo*,3-*exo*-isomer. D, 2-*endo*,3-*endo*-isomer.

and these shifts are different for the various isomers. However, it is not easy to correlate the chemical shifts with structure. In the solutions used, it would be expected that the diamagnetic anisotropy of the pyridine molecules, especially those hydrogen-bonded to

the solute, would result in chemical shifts in the solute which would not occur in an isotropic solvent. Slomp and MacKellar (13) have in fact shown that pyridine can be a useful solvent in inducing chemical shifts between protons which otherwise have accidentally the same chemical shifts. Furthermore, the chemical shifts of the methyl groups differ appreciably when the solvent is wet pyridine instead of dry pyridine.

Protons on C4, C5, and C6 lie mostly to low field of the methyl groups. As these five protons are all different, but are not very chemically shifted from one another, an analysis would be extremely difficult and has not been attempted.

The greatest interest in the spectra lies in the bands (Fig. 4) given by the 2- and 3-protons. In the 2-*exo*,3-*exo*-diol,[2] the bands corresponding to these protons form a symmetrical quartet of the easily recognizable AB type (2, 5). The coupling constants obtained are $J_{23} = 7.7$ c.p.s. and $J_{24} = J_{34} = 0$.

In the other cis isomer, the 2-*endo*,3-*endo*-diol, the bands of the 2- and 3-protons have 12 lines. If one ignores for the moment the two smallest spacings, the pattern can be recognized as that of the AB part of an ABX system (2, 5). From this it is calculated that $J_{23} = 8.0$ c.p.s., $J_{34} = 4.4$ c.p.s., and $J_{24} = 0$. It is extremely unlikely that the alternative assignment of $J_{34} = 0$ and $J_{24} = 4.4$ c.p.s. is correct. The additional spacing present in the bands of the 2-proton might be explained as being due to J_{24}, but this cannot explain the fact that there is a similar spacing in the bands of the 3-proton. In that case there must be coupling of the 3-proton to one proton other than the 2- or 4-proton. None of the protons on the methyl groups can be implicated since the rapid internal rotation of the methyl groups (2) means that three protons would be the minimum number involved, and this could not give rise to the observed splitting. Furthermore, none of the methyl bands shows any sign of splitting.

The most reasonable explanation is that there is a small coupling between *exo*-protons on C2 and C6 and also on C3 and C5. The absence of coupling of the *endo*-protons on C2 and C3 in the 2-*exo*,3-*exo*-diol to either the *exo*- or the *endo*-protons on C6 and C5 (not necessarily respectively) makes it unlikely that in the present case the *exo*-protons on one side of the molecules are coupled with *endo*-protons on the other side. This leaves only the *exo*-protons for consideration. The molecular framework of the [1,2,2]-bicycloheptane system possesses symmetry, so that one would expect that if the 2-*exo*-proton is coupled to the 6-*exo*-proton then the 3-*exo*-proton should be coupled to the 5-*exo*-proton, even though the molecule as a whole has no symmetry. Similarly, if the 2-*exo*-proton is coupled to the 5-*exo*-proton, then the 3-*exo*-proton should be coupled to the 6-*exo*-proton. Of these two possibilities the first is preferable as it involves coupling through a lesser number of bonds.

Although 1,3-coupling does not seem to have been observed previously between protons in saturated systems (5), with the exception of three-membered rings, its presence in the [1,2,2]-bicycloheptane system may reflect the strain present and the closeness of the carbon atoms 2 and 6 and of 3 and 5. As in the case of 1,2-coupling, there is a strong angular dependence for only two *exo*-protons 1,3 to one another are coupled to an observable extent. The values of the coupling constants ($J_{24} = 0$, $J_{2\text{-exo6-exo}} = 1.4$, $J_{3\text{-exo5-exo}} = 1.0$, $J_{3\text{-endo4}} = 0$, $J_{3\text{-exo4}} = 4.4$ c.p.s.) found for the cis isomers should also hold approximately for the trans isomers. It will be assumed that this is so in the analysis of the remaining two spectra.

[2]*The terms exo and endo are used to indicate a substituent cis and trans respectively to the one carbon bridge of the bicycloheptane system. In the naming of the compounds the substituents are, of course, the hydroxyl groups. The terms exo and endo will also be used as required to denote the position of a proton. Thus in the present case the 2- and 3-protons are both endo.*

In the 2-*exo*,3-*endo*-diol the doublet at high field must be due to the 2-*endo*-proton and this gives J_{23} = 2.3 c.p.s. The 3-*exo*-proton at low field is coupled to the 4-proton, and presumably, also to the 5-*exo*-proton. The band obviously contains many unresolved lines, which are most probably due to the 4-proton (and also perhaps the 5-proton) being very little chemically shifted from protons on C5 and C6 to which it is coupled. Nevertheless, we may ascribe the large spacing (ca. 4 c.p.s.) to J_{34}; this will be at least a minimum value.

In the 2-*endo*,3-*exo*-diol the doublet at high field can be assigned to the 3-*endo*-proton. This gives J_{23} = 2.2 c.p.s. and J_{34} = 0. The 2-*exo*-proton gives a wide band, roughly a poorly resolved triplet of intensity 1:2:1, indicating that it is not only coupled to the 3-proton but also to another proton, presumably the 6-*exo*-proton. The poor aspect of the band can again be ascribed, as for the 3-*exo*-proton of the previous isomer, to insufficient chemical shift between the 6-*exo*-proton and other protons on C5 and C6.

The chemical shifts of the 2- and 3-protons of the camphane-2,3-diols are difficult to correlate with structure and this difficulty is at least partly due to the reasons previously mentioned in the case of the chemical shifts of the methyl groups. The τ values of the 2- and 3-protons (Fig. 3) are close to the value (6.15) for CH groups of secondary alcohols (5), but exact comparisons cannot be made because pyridine is used as the solvent in the present case.

The observed coupling constants and those calculated from the dihedral angles (Table I) and Karplus' data (8) are given in Table II. The dihedral angles in Table I were

TABLE I

Dihedral angles in the camphane system

CH bonds	Dihedral angle
2-*exo* and 3-*exo*	0°
2-*endo* and 3-*endo*	0°
2-*exo* and 3-*endo*	ca. 120°
2-*endo* and 3-*exo*	ca. 120°
3-*endo* and 4	ca. 79°
3-*exo* and 4	ca. 44°

TABLE II

Observed and calculated coupling constants (in c.p.s.) for the camphane-2,3-diols

	J_{23}		J_{34}		J_{26}	J_{35}
Diastereoisomer	Obs.	Calc.	Obs.	Calc.	Obs.	Obs.
2-*exo*,3-*exo*	7.7	8.2	0	0	0	0
2-*exo*,3-*endo*	2.3	2.1	ca. 4.0	4.1	?	0
2-*endo*,3-*exo*	2.2	2.1	0 (?)	0	0	?
2-*endo*,3-*endo*	8.9	8.2	4.4	4.1	1.4	1.0

obtained by measurements made on Barton molecular models. Some bending of the bonds is required to make the models and this results in a change of bond angles from the tetrahedral value. Some of the dihedral angles are uncertain because it is not known exactly how the distortion is spread through the molecule. In the model all bonds are slightly bent so that the strain is distributed more or less uniformly. The uncertainties in dihedral bond angles are most unlikely to affect the conclusions made in this paper.

The distortion of the molecule does not change the 0° dihedral angles, but does increase, for example, the dihedral angle which would have been 120° otherwise. Unfortunately, no very accurate structure determination seems to have been carried out in the [1,2,2]-bicycloheptane series. The structure of 3-cyanocamphor has been determined (14) but the positions of all the atoms are not accurately known. The [1,2,2]-bicycloheptane system can be considered as two fused five-membered rings. Each ring is approximately in the C_s (15) or envelope (16) conformation. The assumption of complete (or almost complete) eclipsing of carbons 2 and 3 is probably a good one in this case, as any staggering increases the considerable strain already present.

The results shown in Table II also agree with coupling constants found in α- and α'-chlorocamphor (17). In the α-isomer the 3-proton, which is *exo*, is coupled to the 4-proton by 5 c.p.s., whilst in the α'-isomer, where the 3-proton is *endo*, J_{34} is zero. Similarly, in 3,8-cyclocamphor (18) the coupling constant of the 3-*endo*-proton to the 4-proton is zero.

The very good agreement between calculated and observed coupling constants found in Table II is strong support for the validity of Karplus' calculations. It is to be noted that coupling constants in three-membered and four-membered rings (5, 19, 20) do not agree very well with those expected from Karplus' work, in contrast to the situation which exists in most five- and six-membered rings.

It is obvious from the results presented here that in non-rigid cyclopentane derivatives (15, 16) the coupling constants will depend very markedly on the conformation(s) which the molecules adopt. If the stereochemistry and coupling constants are known, it may become possible to deduce the conformation of such rings. In fact, attempts to do this have already been made by Jardetzky (9) in the case of the ribose nucleosides and nucleotides. The conclusions drawn in that paper derive support from the present work.

ACKNOWLEDGMENTS

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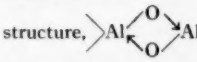
REACTIONS OF ALUMINUM ALKOXIDES WITH ACETYLACETONE, BENZOYLACETONE, AND ETHYL ACETOACETATE[1]

R. K. MEHROTRA AND R. C. MEHROTRA

ABSTRACT

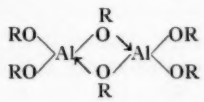
The observed stability of stable bridge structure,  , in aluminum alkoxides has been explained on the powerful tendency of aluminum to attain co-ordination number 4. This would predict the monomeric nature of the derivatives of the type, $(OR)_2Al(lig)$, where ligand (lig) is a diketone like acetylacetone (acac), benzoylacetone (bzac), or ketoester like ethyl acetoacetate (etac). This has been confirmed by actual synthesis of these compounds by reactions between aluminum alkoxides (ethoxide and isopropoxide) and acetylacetone, benzoylacetone, and ethyl acetoacetate in equimolecular ratios. These and also $(OR)Al(lig)_2$ as well as $Al(lig)_3$ have been shown to be monomeric in boiling benzene. The volatility of the derivatives was found in the order $[(OPr^i)_3Al]_2 > (OPr^i)_2Al(acac) > (OPr^i)Al(acac)_2$. This leads to the conclusion that chelation lowers the volatility and the direct relationship between volatility and molecular complexity, observed in the case of simple alkoxides, is not applicable in these derivatives. Further mixed derivatives of the type $Al(acac)(etac)_2$ and $Al(etac)(acac)_2$ have also been synthesized during the course of the above work.

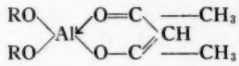
INTRODUCTION

Aluminum alkoxides are generally prepared by the reaction of corresponding alcohols with metallic aluminum with the help of catalysts (1). Mehrotra (2, 3) described the preparation of higher aluminum alkoxides by treating aluminum ethoxide and isopropoxide with the corresponding alcohol and removing the ethanol or isopropanol produced, azeotropically with benzene. The technique has now been extended to prepare acetylacetonate, benzoylacetonate, and ethyl acetoacetate derivatives of aluminum by the simple reactions of the type:

$$Al(OR)_3 + x\text{H lig} \rightarrow Al(OR)_{3-x}(lig)_x + x\text{ROH}$$

(where ligand is acetylacetone, benzoylacetone, or ethyl acetoacetate).

The main interest of the above study arose from earlier observations of one of us (2), that the bridge structure  is very stable in aluminum alkoxides and exists even in the vapor phase. On aging, alkoxides were shown to exhibit greater molecular complexity (2) and this phenomenon has been explained by Bradley (4) to be due to the tendency of 4-co-ordination aluminum to change to the 6-co-ordination. In view of the above, it was conjectured that a monosubstituted product like $Al(OR)_2(lig)$ should be monomeric as co-ordination number 4 would be easily satisfied in the structure:



The above has been confirmed for the mono acetylacetone, benzoylacetone, and ethyl acetoacetate products with R as C_2H_5 (Et) or C_3H_7 (Pr^i). The derivatives further do not show any tendency of polymerization, even after aging for a few weeks. The di and tri derivatives have also shown to be monomeric in benzene. It is of particular interest

[1]*Manuscript received November 25, 1960.*
Contribution from the Chemical Laboratories, University of Gorakhpur, Gorakhpur, U.P., India.

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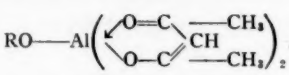
to note that the di derivatives would have a co-ordination number 5 as depicted by the following simple structure:



A point of further interest was the volatility of the above derivatives. This was of special interest as in a number of aluminum (2), titanium, zirconium (5), and other alkoxide derivatives, it has been shown that the decreasing volatility has, in general, a simple relationship with increasing molecular complexity or weights. The above derivatives could be distilled at higher temperatures compared to aluminum alkoxides, indicating that the chelation has the expected effect of lowering the volatility and overcomes the opposite effect of simpler molecular complexity.

EXPERIMENTAL

Materials

Aluminum ethoxide was prepared by the method of Chalmers (6). Aluminum isopropoxide was prepared as described by Young, Hartung, and Crossley (7). Both were purified by distillation under reduced pressure.

Acetylacetone and ethyl acetoacetate (E. Merck) were dried by refluxing with aluminum isopropoxide and fractionating. Benzoylacetone was synthesized (8) and purified by distillation.

Benzene (B.D.H.) was dried by distilling over metallic sodium and carefully fractionated before use.

All glass apparatus fitted with interchangeable joints was used throughout and special precautions were taken to exclude the moisture. Fractionations were carried out in a column packed with Raschig rings.

Analytical Methods

Aluminum was determined as oxinate gravimetrically except in benzoylacetonate derivatives in which cases ignition to oxide was employed.

The amount of alcohol in benzene–alcohol azeotrope was estimated by a back titration method of Bradley and Wardlaw (9).

Alkoxy group in the presence of acetylacetone, benzoylacetone, or ethyl acetoacetate was estimated by liberating the isopropanol or ethanol from the compound by boiling it in benzene with an excess of acetylacetone or ethyl acetoacetate and subsequently estimating the ethanol or isopropanol liberated in benzene alcohol azeotrope.

Molecular Weights

The molecular weights of compounds were determined ebullioscopically in boiling benzene by using a Gallenkamp ebulliometer with a sensitive transistor principle. The elevations (ΔT) were plotted against the weight of solute added and in all cases a straight line was obtained. The constant K for the solvent was determined with naphthalene. The results are recorded in Table I.

Synthetic Reactions

The general method of synthesis was the same in every case and so the details will be given only for acetylacetone compounds with aluminum isopropoxide and mixed acetylacetone – ethyl acetoacetate derivatives. In cases of all other derivatives described in Table II, the method was the same as with acetylacetone derivatives; the amount of alcohol collected in the azeotrope was, within experimental error, equal to the amount expected from the stoichiometry of the reaction. The yields of the pure distilled or crystallized derivatives are also included in Table II.

TABLE I

Results of molecular weight determination

No.	Formula of the compound	Concn. range (g), per 15 cc of benzene	Molecular weight	
			Found	Calcd.
1.	$Al(OEt)_2(acac)$	.102–.274	209	216
2.	$Al(OEt)_2(etac)$	.094–.431	261	246
3.	$Al(OEt)_2(bzac)$	.058–.227	262	278
4.	$Al(OEt)(acac)_2$	.124–.453	297	270
5.	$Al(OEt)(bzac)_2$	.052–.168	412	394
6.	$Al(OEt)(etac)_2$	.116–.292	344	330
7.	$Al(OPr^i)_2(acac)$	.062–.162	253	244
8.	$Al(OPr^i)_2(bzac)$	.041–.173	293	306
9.	$Al(OPr^i)_2(etac)$	.217–.471	283	274
10.	$Al(OPr^i)(acac)_2$	.046–.198	275	284
11.	$Al(OPr^i)(bzac)_2$	.058–.158	388	408
12.	$Al(OPr^i)(etac)_2$	.165–.564	360	344
13.	$Al(acac)_3$	.087–.336	316	324
14.	$Al(bzac)_3$	.080–.287	501	510
15.	$Al(etac)_3$	.102–.306	425	414

TABLE II

Properties of the compounds

No.	Formula	Appearance	% yield of distilled or purified compound	B.p.	Analyses			
					Al%		OR %	
					Found	Calcd.	Found	Calcd.
1.	$Al(OEt)_2(acac)$	Yellow liquid	96	188°/4 mm	12.52	12.49	41.2	41.6
2.	$Al(OPr^i)_2(acac)$	Yellow solid	81	160°/5 mm	11.18	11.06	47.6	48.3
3.	$Al(OEt)(acac)_2$	Yellow crystals	95	—	10.2	10.0	16.1	16.6
4.	$Al(OPr^i)(acac)_2$	Yellow crystals	96	—	9.38	9.5	19.6	20.7
5.	$Al(OEt)_2(bzac)$	Yellow crystals	95	—	9.9	9.7	31.6	32.3
6.	$Al(OPr^i)_2(bzac)$	Yellow crystals	97	—	8.9	8.8	39.1	38.5
7.	$Al(OEt)(bzac)_2$	Yellow crystals	97	—	6.9	6.8	11.0	11.4
8.	$Al(OPr^i)(bzac)_2$	Yellow crystals	97	—	6.53	6.61	13.7	14.4
9.	$Al(OEt)_2(etac)$	Yellow liquid	98	200°/5 mm	10.79	10.9	35.8	36.5
10.	$Al(OPr^i)_2(etac)$	Yellow liquid	94	205°/10 mm	9.83	9.80	44.6	43.06
11.	$Al(OEt)(etac)_2$	Yellow liquid	82	188°/3 mm	8.10	8.17	14.07	13.6
12.	$Al(OPr^i)(etac)_2$	Yellow liquid	67	225°/10 mm	7.7	7.8	17.3	17.1
13.	$Al(acac)_3$	Yellow crystals	91	—	8.5	8.32	—	—
14.	$Al(bzac)_3$	Yellow crystals	95	—	5.40	5.29	—	—
15.	$Al(etac)_3$	Yellow powder	93	—	6.80	6.51	—	—
16.	$Al(acac)(etac)_2$	Yellow semisolid	94	—	7.18	7.02	—	—
17.	$Al(etac)(acac)_2$	Yellow mass	94	—	7.7	7.6	—	—

I. Reaction of Aluminum Isopropoxide with Acetylacetone in Molar Ratio of 1:1

Acetylacetone (3.28 g) was added to a solution of aluminum isopropoxide (6.70 g) in dry benzene (60 g). Heat was evolved during mixing of reactants. The mixture was refluxed for 3 hours at bath temperature of 120–30°. Benzene–isopropanol azeotrope was distilled slowly between 72–80°, followed by benzene, leaving a yellow liquid in the reaction flask. No crystallization occurred even after standing overnight. The remaining benzene was distilled out under reduced pressure and the compound was distilled at 160°/5 mm to give a light yellowish mobile liquid (6.5 g) which solidified on being kept for 3–4 days. The total amount of isopropanol in the azeotrope was found to be 1.90 g against 1.97 g, calculated for 1 mole. (Found: Al, 11.18; OPr^i, 47.6. Calcd. for $Al(acac)(OPr^i)_2$: Al, 11.06; OPr^i, 48.3%.)

II. Reaction of Aluminum Isopropoxide with Acetylacetone in Molar Ratio of 1:2

Acetylacetone (5.89 g) was added to a solution of aluminum isopropoxide (6.01 g) in benzene (80 g). Heat was evolved. The mixture was refluxed for 4 hours and the benzene–isopropanol azeotrope was taken between 72–80°. Pure benzene was distilled out till a light yellowish residue was left. On cooling it gave crystals (8 g) which were dried under reduced pressure for 3 hours. The total amount of isopropanol found in the azeotrope was 3.35 g, against 3.46 g, calculated for 2 moles. (Found: Al, 9.38; OPr^i, 19.6. Calcd. for $Al(OPr^i)(acac)_2$: Al, 9.5; OPr^i, 20.7%.)

The above compound was sublimed at a bath temperature of 300°/5 mm to give a yellowish mass (Found: Al, 9.34%).

III. Reaction of Aluminum Isopropoxide with Acetylacetone in Molar Ratio of 1:>3

Acetylacetone (12.56 g) was added to a solution of aluminum isopropoxide (7.6 g) in benzene (80 g) and the mixture refluxed for 3 hours. Benzene–isopropanol azeotrope was taken out slowly. Afterwards, pure benzene was distilled out, till a light yellowish liquid remained in the reaction flask which on cooling gave crystals. Total amount of isopropanol was found to be 6.6 g, against 6.7 g, calculated for 3 moles, in the azeotrope. (Found: Al, 8.5. $Al(acac)_3$ requires Al, 8.33%.)

IV. Reaction of Aluminum Diisopropoxy Monoacetylacetonate with Ethyl Acetoacetate in Molar Ratio of 1:2

Ethyl acetoacetate (2.34 g) was added to a solution of aluminum diisopropoxy monoacetylacetonate (2.19 g) in benzene (50 g). The mixture was refluxed for 2 hours. Benzene–isopropanol azeotrope was collected slowly between 72–80°; followed by pure benzene leaving a yellow liquid in the reaction flask, which was dried under reduced pressure at 50° to give a yellow semisolid (3.2 g). The total amount of isopropanol in the azeotrope was found to be 1.1 g against 1.07 g calculated for 2 moles. (Found: Al, 7.18. Calcd. for $Al(etac)_2(acac)$, 7.02%.)

V. Reaction of Aluminum Diisopropoxy Monoethyl Acetoacetate with Acetylacetone in Molar Ratio of 1:2

Acetylacetone (3.26 g) was added to a solution of aluminum diisopropoxy monoethyl acetoacetate (4.45 g) in benzene (50 g). Heat was evolved as a result of reaction. The mixture was refluxed for 2 hours and the benzene–isopropanol azeotrope was taken between 72–80°. Pure benzene was distilled out till there was left a yellow liquid which was dried under reduced pressure for 4 hours to give a yellow mass (5.5 g). The total amount of isopropanol was found to be 1.9 g, against 1.94 g required for 2 moles. (Found: Al, 7.7. Calcd. for $Al(etac)(acac)_2$, 7.6%.)

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POTASSIUM DERIVATIVES OF FLUORENE AS INTERMEDIATES IN THE PREPARATION OF C_9-SUBSTITUTED FLUORENES

III. THE INFLUENCE OF SOLVENT AND METAL IN THE FORMATION OF C_9-SUBSTITUTED FLUORENES FROM 9-FLUORENYL METALS[1]

G. W. H. Scherf and R. K. Brown

ABSTRACT

Equimolar quantities of 9-fluorenyl-potassium, -sodium, or -lithium and alkyl or aralkyl halides at room temperature in ether solvents yielded a mixture of unchanged fluorene, C_9-monosubstituted fluorene, and C_9-disubstituted fluorene. The amount of disubstitution never exceeded that of unchanged fluorene, and was found to be maximum (~35%) for the potassium compound in 1,2-dimethoxyethane, somewhat less for the sodium analogue, and small (~5%) for the lithium compound. In hydrocarbon solvents such as hexane, 9-fluorenylpotassium gave only 7% of C_9-disubstituted fluorene. The lithium compound, upon reaction with methyl iodide or ethyl iodide gave, along with unreacted fluorene, only C_9-monosubstituted fluorene. But reaction of 9-fluorenyllithium with benzyl chloride in hexane gave a small quantity (~5%) of disubstituted fluorene as well as the monosubstituted product.

The results are explained in terms of (*a*) the solubilities of the organometallic compounds in ether and hydrocarbon solvents, (*b*) the polarity of the metal carbon bond, and (*c*) the acidity of the hydrogen on C_9 of fluorene.

INTRODUCTION

A recent publication described the infrared spectra of a number of C_9-mono- and -di-substituted fluorenes (1). For the infrared work the 9,9-disubstituted fluorenes were prepared by treating one mole of fluorene in dioxane with two gram equivalents of potassium metal. The metalated product was then brought into reaction with two moles of the appropriate halide. Contaminating monosubstituted and unsubstituted fluorene was then removed either by crystallization, or by chromatography.

Attempts to prepare C_9-monosubstituted fluorene from the reaction between equimolar proportions of fluorene and potassium in dioxane, followed by the addition of an equivalent amount of alkyl or aralkyl halide led to a mixture of C_9-monosubstituted, C_9-disubstituted, and unsubstituted fluorene whose separations were frequently somewhat tedious for routine synthesis. Accordingly, the C_9-monosubstituted compounds required for the absorption studies were prepared more conveniently by the procedure developed by Greenhow, White, and McNeil (2).

This paper describes the results of a study of mono- versus di-substitution at carbon 9 of fluorene when 9-fluorenyl-lithium, -sodium, or -potassium was allowed to react with an equimolar quantity of an alkyl or aralkyl halide in the solvents hexane (or heptane), dioxane, 1,2-dimethoxyethane (DME), 1,2-diethoxyethane (DEE), and tetrahydrofuran (THF).

RESULTS

The Reaction of 9-Fluorenylpotassium with Alkyl and Aralkyl Halides in Ether and Hydrocarbon Solvents

The 9-fluorenylpotassium required for this work was prepared from equimolar amounts of potassium and fluorene (1). This could be readily isolated and transferred to the solvent chosen for study.

[1]*Manuscript received September 12, 1960.*
Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta. Taken from the thesis of G. W. H. Scherf to be submitted to the Graduate School of the University of Alberta in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Two outstanding differences were observed between the reactions at room temperature of 9-fluorenylpotassium with organic halides in *ether* solvents and its reaction with these halides in hydrocarbon solvents. *Firstly*, when dioxane, diethyl ether, diisopropyl ether, or di-*n*-butyl ether was the solvent, reaction of the organometallic compound with the organic halide was relatively fast. Within 5 minutes nearly all of the solid suspension of 9-fluorenylpotassium had disappeared. On the other hand, when *n*-heptane was the suspending solvent, much of the 9-fluorenylpotassium was still unchanged after an interval of 30 minutes. The marked difference in the rate of reaction was no doubt due to the partial solution of the 9-fluorenylpotassium which occurred in the ethers but not in heptane. This was borne out by the observation that the depth of the reddish color of the ether solution could be correlated, if only roughly, with the rate of reaction when, for the experiments concerned, equivalent quantities of reagents were used. No color was observed in the solvent for the heptane suspension, hence, in this medium, the reaction with the halide is considered to occur heterogeneously on the surface of the suspended solid, resulting in a much slower reaction dependent in part upon diffusion rate and efficiency of stirring. *Secondly*, reaction of 9-fluorenylpotassium with an organic halide in molar ratio 1:1 in *ethers* gave considerable quantities of 9,9-disubstituted fluorene along with C_9-monosubstituted and also unchanged fluorene while the same reaction in *heptane* gave essentially monosubstitution with relatively little 9,9-disubstituted fluorene. The amount of disubstituted material obtained from the reaction in dioxane was about 25% of the fluorene originally used to form the potassium compound and fell somewhat short of equivalence to the amount of unchanged fluorene. This extra quantity of fluorene most likely was that which had originally failed to react with the metal. From an examination of the results of alkylation in dioxane solvent with methyl iodide, ethyl bromide, allyl bromide, and benzyl chloride, the ratio of disubstitution to monosubstitution appears to be independent of the size of the alkyl or aralkyl group (Table I).

TABLE I

Conversion of fluorene into the mono- and di-substituted derivatives by reaction of 9-fluorenylpotassium with various alkyl halides in dioxane solvent

Alkyl halide	% disubstitution	% monosubstitution	% fluorene
Methyl iodide	26	43	31
Ethyl bromide	27	43	30
Allyl bromide	27	40	33
Benzyl chloride	23	(*)	(*)

*Accurate amounts unknown since quantitative separation of the monobenzylfluorene from fluorene was not achieved either by crystallization or chromatography.

With heptane as solvent, only about 5% of the original fluorene was converted to 9,9-disubstituted fluorene while the quantity of C_9-monosubstituted product actually isolated was 75 to 85%. The remainder of the product was unchanged fluorene.

The characteristic absorption bands used to identify the presence of C_9-mono- and C_9-di-substitution (1) and to follow the extent of separation are given in Table II. The absorption spectra of 9-ethylfluorene and 9,9-diethylfluorene, previously unreported (1) are shown in Figs. 1 and 2. The small region from 1050 to 1110 cm^{-1} is quite helpful for the determination of mono- versus di-methylfluorene. The absorption is not intense but quite sharp and distinct. Dimethyl fluorene shows a band at 1078 cm^{-1} (with a smaller one at 1085 cm^{-1}). Monomethylfluorene shows no absorption at these positions

TABLE II

Characteristic absorption bands in the infrared for C_9-substituted fluorenes (cm^{-1})

Methyl		Ethyl†		Benzyl		Allyl	
mono-	di-	mono-	di-	mono-	di-	mono-	di-
		658 m	Nil				
						681 mw*	681 mw*
				700 s*	700 s*		
719 m	Nil	Nil	Nil				
				Nil	720 ms		
						727 ms	Nil
		735–40 (broad)	735–40 (narrow)				
				746–48	746–48		
				754 s	Nil	754 s	—
758 s*	758 s*						
				Nil	761–64 s	—	761–64 s
793 s	Nil	Nil	Nil				
Nil	Nil	820 w	Nil				
Nil	Nil	838 w	Nil				
		869 mw*	869 mw*				
				905–9 m*	905–9 w		
						913 s*	913 s*
			925 m*				
932 m	932 m						

m = medium; s = strong; w = weak

*The disubstituted compounds absorb approximately twice as much as do the monosubstituted fluorenes and have broader bands.

†In addition, the monoethyl compound shows two strong bands at 748 cm^{-1} and 760 cm^{-1}, the former more intense than the latter. The diethyl compound shows strong adsorption at 754 cm^{-1} and 760 cm^{-1} the latter stronger than the former.

but in turn exhibits sharp though weak absorption at 1098 cm^{-1}. Fluorene absorbs only at 1089 cm^{-1} in this region (Fig. 3).

Influence of Solvent and Metal in C_9-Mono- and -Di-substitution

Table III shows the results of the reaction of methyl iodide and 9-fluorenylpotassium

TABLE III

Products of the reaction of equimolar amounts of 9-fluorenylpotassium and methyl iodide in various solvents

Solvent	Time§ (hr)	Apparent extent of metalation	Dimethyl-fluorene, %	Mono-methyl-fluorene, %	Fluorene, %
DME	1	Complete	35	30	35
DEE	1–2	Complete	25	22	53
THF	4	Complete	20	20	60
Dioxane	4	Complete	25	40	35
Toluene–DME*	4	Complete	20	20	60
Toluene–DEE*	4	Complete	—	—	—
Toluene–THF*	4	Complete	10	25	65
Toluene–dioxane*	4	Incomplete	5	40	55
Heptane–DME*†	3	Complete	33	30	37
Hexane or heptane‡	4	—	7	40	53

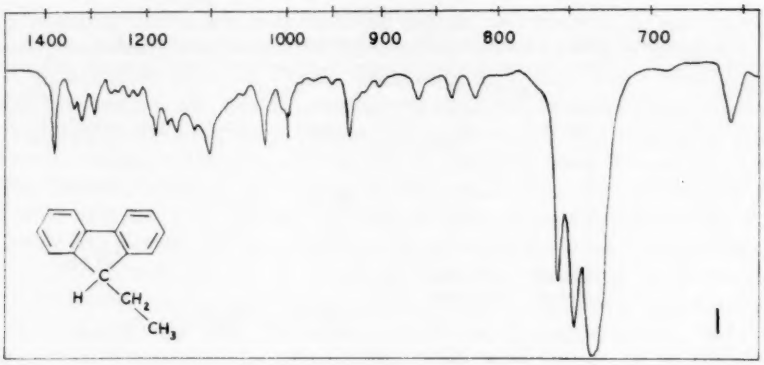
*The ratio of ether to toluene was 1:4 by volume.

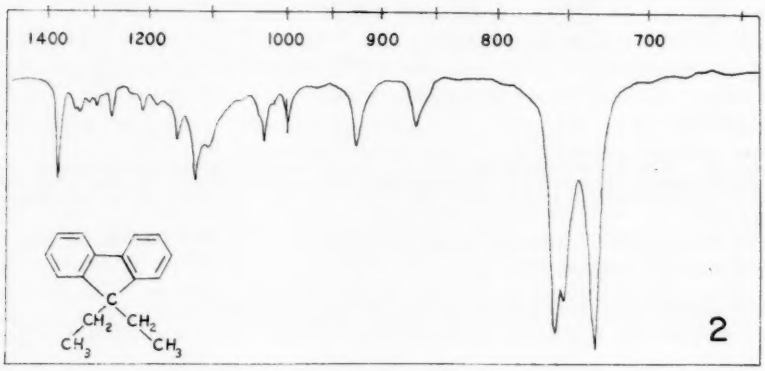
†Two layers were formed during the reaction, the lower one containing the ether and the metal organic compound (ref. 3).

‡The potassium fluorenyl was prepared in dioxane, isolated by filtration, and suspended in the hydrocarbon for the reaction with CH_3I.

§The time allowed for the formation of the organometallic compound at reflux temperature of the solution.

in cyclic- and poly-ethers, in hydrocarbons, and in mixtures of ethers and hydrocarbons. In Tables IV and V are listed the results of similar reactions of the sodium and lithium analogues with methyl iodide.





FIGS. 1 and 2.

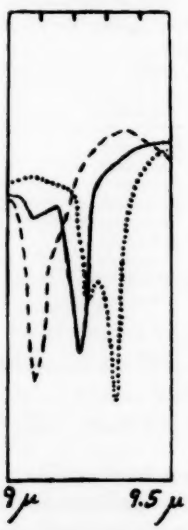


FIG. 3. The 9μ to 9.5μ region (1110 cm^{-1} to 1050 cm^{-1}) of the infrared spectrum of fluorene ———, 9-methylfluorene – – – –, and 9,9-dimethylfluorene . . . . . , taken in CS_2 solution.

TABLE IV

Products of the reaction of equimolar amounts of 9-fluorenylsodium and methyl iodide in various solvents

Reagent	Solvent	Time* (hr)	Apparent extent of metalation	Dimethyl-fluorene, %	Mono-methyl-fluorene, %	Fluorene, %
Na	DME	36	Complete	35	30	35
Na	DEE	40–50	Incomplete	20	40	40
Na	THF	48	†			
Na	Dioxane	36	‡			
$NaNH_2$	DME	3	Incomplete	15	40	45
$NaNH_2$	Dioxane	3	See experimental	10	35	55
	n-Heptane	§		None found	65	35

*Time allowed for the reaction between the metal or amide and fluorene in the refluxing solvents.
†The metalation with sodium metal was incomplete in all cases (ref. 3).
‡The extent of metalation was too small for separation of products.
§The sodamide was allowed to react with fluorene in refluxing dioxane for 3 hours. The precipitate was removed from the cooled solution, washed free of dioxane with hexane, and suspended in heptane.

TABLE V

Products from the reaction of equimolar amounts of 9-fluorenyllithium and methyl iodide in various solvents

Solvent	Time*	Apparent extent of metalation	Dimethyl-fluorene, %	Mono-methyl-fluorene, %	Fluorene, %
DME	4–5	Complete	5	80–85	15–10
DEE	5–6	Complete	5	60	35
THF	8	Complete	1–2	~85	14–13
Hexane†	—		0	80	20

*Time allotted for the formation of the organometallic compound in the refluxing solvent.
†9-Fluorenyllithium was prepared in DEE, then isolated, suspended in hexane, and treated with methyl iodide.

In general, it can be seen that in dimethoxyethane (DME), diethoxyethane (DEE), and tetrahydrofuran (THF), 9-fluorenylpotassium and 9-fluorenylsodium, treated with equimolar amounts of methyl iodide, gave from 20 to 35% disubstitution. In addition, at *least* the same amount of unreacted fluorene was formed along with 20 to 40% of monosubstitution. The efficiency of the solvent in promoting conversion to the dimethylated product is, in decreasing order, DME > DEE > THF. This is the same solvent order which was found previously in the study of the influence of solvent on the extent of reaction of potassium with fluorene (3). Hydrocarbon solvents, or ethers mixed with hydrocarbon solvents, generally gave less dimethylation but somewhat more monomethylation than was found when the pure ethers were used.

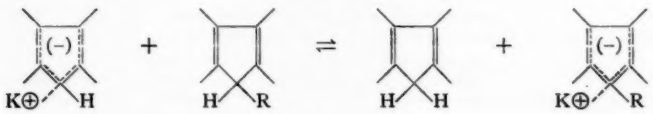
The exception was the reaction of 9-fluorenylpotassium with methyl iodide in a mixture of heptane and DME (Table III). However, that one obtained results similar to those found when pure DME was employed, can be explained. When the metal had reacted with the fluorene in this mixed solvent, two liquid layers appeared—the lower being essentially that due to the ether containing 9-fluorenylpotassium, while the upper was primarily heptane contaminated with some DME but containing no 9-fluorenylpotassium. Hence, the lower layer, where further reactions with methyl iodide occurred, approximated the conditions which held in the case where the solvent was DME only.

The 9-fluorenyllithium (prepared by precipitation from cold DEE (3)) treated with an equimolar amount of methyl iodide, gave little or no dimethylation in ether or hydrocarbon solvents. In all cases a high yield of monosubstituted fluorene was obtained.

DISCUSSION

The results of the reaction of 9-fluorenyl-lithium, -sodium, or -potassium can be rationalized on the basis of (*a*) the insolubility of the organometallic compound in hydrocarbons such as hexane, but solubility, though limited in some cases, in ethers, (*b*) the relative electropositive nature of the three metals thus giving rise to both the ionic character and reactivity of the carbon–metal bond in fluorene in the order K—C > Na—C > Li—C, (*c*) the acidic properties of fluorene and C_9-monosubstituted fluorenes.

In non-polar and non-ionizing solvents such as hexane, all three alkali metal salts possess closely associated cations and anions having a considerable amount of covalent character in the metal–carbon bond. The degree of covalency is expected to be in the order Li > Na > K. The reaction of the organic halide (RX) in hexane occurs by attack at the surface of the insoluble and suspended solid. The more polar C—K bond should react with the organic halide more quickly than does the C—Li bond. The monosubstituted fluorene, as soon as it is formed, can escape from the surface of the solid into solution. However, if the newly formed 9-monosubstituted fluorene possesses an acidic hydrogen, there will occur on the surface of the solid a reaction such as shown in A



A

between this product and more of the salt, the extent of which depends upon the acidity of the monosubstituted fluorene. This would lead to disubstitution after further reaction with the alkyl halide. Since little or no disubstitution occurred in the reaction of 9-fluorenyl-lithium, and very little 9,9-disubstituted fluorene was formed when the potassium and sodium analogues reacted with alkyl or aralkyl halides in hexane or heptane, it is apparent that the polar halide was absorbed from the solution and reacted with the organometallic compound much more readily than did the 9-monoalkylated fluorene which escaped into solution before it reacted further. The small amount of disubstituted fluorene actually observed in the case of the potassium salt in hexane arose no doubt from a scheme such as that suggested in reaction A due to the greater ionic character of the K—C bond.

The electron-donor properties of ethers, however, causes some of the salt to be soluble in some cases (e.g. dioxane) while most or all of the alkali metal compound is dissolved in others (e.g. DME). In solution, because of this association of the ether and the organometallic compound (3), the ionic character of the metal–carbon bond is increased—more so for the more electropositive metals potassium and sodium than for the lithium. Reaction in solution between the salt and the organic halide therefore is expected to, and actually did, occur more rapidly. The newly formed 9-monosubstituted compound, which is also in solution, is thus able to set up an equilibrium similar to that shown in A but involving the solvated organometallic compound and that portion of the 9-fluorenyl metal as yet unreacted. The 9-alkyl-9-fluorenyl-potassium (-sodium or -lithium) can then react with a second molecule of the organic halide to give the disubstituted fluorene. Thus, there is produced one molecule of unchanged fluorene for every molecule of disubstituted fluorene. In all our experiments, there has been no case where more disubstituted than unsubstituted product has been produced, in agreement with the reaction

shown in A. The position of equilibrium will then depend upon the relative acidities of the fluorene and monosubstituted fluorene and upon the rapidity with which the organic halide reacts with the monometalated fluorene. The assumption that disubstitution is obtained via the above equilibrium occurring primarily *in solution* is supported by the greater extent of disubstitution actually found in solvents wherein almost all, if not all, the organometal was dissolved (Tables III and IV). Since the lithium derivative gave very little disubstitution in any solvent (Table V), even in those wherein it is quite soluble, it is obvious that the extent of ionic character of the carbon–metal bond is an important factor which establishes the degree to which such an equilibrium as portrayed by A can be established in competition with the direct reaction of the monometalated compound with the alkyl halide. Usually alkylation at a carbon atom reduces the acidity while arylation increases the acidity of the remaining hydrogen(s) at the same carbon atom. The greater acidity of 9-phenylfluorene over that of fluorene has been recorded (4, 5), but to our knowledge no report compares the acidity of 9-alkylated fluorenes with that of the parent substance. Since disubstitution was actually observed in this work, especially in the case of the more effective ethers, the acidity of 9-alkylfluorenes should be at least of the same order as, but is more likely greater than, that of the unsubstituted fluorene. The tendency of the C_9-substituent to become coplanar with the planar fluorene molecule would lend stability to the 9-substituted fluorenyl anion. A substituent on C_9 may prefer this coplanar arrangement due to steric factors and thus enhance the acidity of the C_9—H. Furthermore, the acidity of the 9-monoalkylated fluorene must be greater than that of fluorene to compete as successfully as it does with the polar bond in the organic halide for the organometallic compound. That the 9-monoalkylated compound should be more acidic than is fluorene due to steric considerations, is not clearly shown from the results of the reaction of 9-fluorenylpotassium with the halides, methyl iodide, ethyl bromide, allyl bromide, and benzyl chloride in dioxane (Table I) since approximately the same extent of disubstitution occurred in each regardless of the size of the group. This lack of differentiation might be due to the highly reactive and therefore less discriminating, K—C bond. But the results of reaction of the 9-fluorenyllithium and 9-fluorenylsodium with methyl iodide and benzyl chloride do support this point of view. Equimolar mixtures of 9-fluorenylsodium and benzyl chloride gave 16% of the 9,9-disubstituted fluorene while only 10% of the dimethylated fluorene was obtained when the halide was methyl iodide. In the case of 9-fluorenyllithium, although reaction with methyl iodide in hexane gave no detectable disubstituted fluorene, nearly 5% of dibenzylfluorene was obtained from the reaction of the lithium salt with benzyl chloride in hexane. The question of the relationship of the size of the C_9-substituent and the ratio of di- to mono-substituted product obviously requires further study.

There exists the possibility that some, if not all, of the disubstitution might be due to unreacted metal, occluded in the organometallic compound, which would react with the monosubstituted fluorene during the process of the addition of the alkyl halide. A report is to be found in the literature that describes such a highly dispersed state of potassium metal in a solvent so as to render it indiscernible to the eye when the solution is cooled (6). Our rate of stirring certainly would not lead to such an ultrafine state of division of the metal—hence any substantial quantity of it which remained unreacted should be readily seen. In order to determine if the presence of unreacted metal actually does play a part in producing disubstituted fluorene, an experiment was performed in which the reaction between equimolar quantities (0.05 mole) of fluorene and potassium in 50 ml of DME was allowed to proceed for just 15 minutes. To the mixture, containing

definitely some unreacted potassium, was added 0.05 mole of methyl iodide. By chromatography of the isolated solid on alumina using hexane as eluant, there was obtained 30% dimethylfluorene, 18% monomethylfluorene, and the remainder as unchanged fluorene. Since the experiments in which all the metal had apparently reacted to form 9-fluorenylpotassium gave 35% di- and 30% mono-methylfluorene, the conclusion must therefore be made that in those cases where unreacted metal does remain, the metal does cause dialkylation, somewhat more readily than in those reactions where only 9-fluorenylpotassium is present. This requires that the monomethylfluorene be more acidic than is fluorene. However, in those solutions where complete reaction of the metal with fluorene has occurred, dialkylation would proceed via an exchange such as shown in equation A.

In this connection, attempts to increase above 65% the yields of dialkylated fluorene, from the reaction with alkyl halides of the "9,9-fluorenyldipotassium" reported in the first of this series of articles (1), have met with consistent failure. Further experimentation has shown that the first atom of potassium reacted with fluorene to produce 9-fluorenylpotassium and an equivalent amount of hydrogen. However, treatment of the 9-fluorenylpotassium with a second equivalent of potassium in dioxane evolved *no hydrogen*. The metal, finely dispersed in the precipitated 9-fluorenylpotassium could not be readily perceived as unreacted metal. However, the reaction of two equivalents of potassium metal with one of fluorene in *DME* gave a clear solution of 9-fluorenylpotassium. Under these conditions the second equivalent of potassium remained unreacted and could be clearly seen suspended in the solvent if less vigorous stirring was employed. The existence of this second equivalent of potassium as unreacted metal, which would then react competitively with the alkyl halide and with the monoalkylated product, probably more rapidly with the former than with the latter, would thus account for the inability to produce more than 65% yield of 9,9-dialkylated fluorene (1). If this is so then at least some of the disubstituted fluorenes observed in the present work could arise from direct interaction of the monoalkylated fluorene and the residual metal in those cases of incomplete metalation.

EXPERIMENTAL

The various alkali metal salts of fluorene were prepared essentially according to published procedures (1, 3). For the present experiments a mixture of 0.05 mole of the metal, and 0.05 mole of fluorene in 50 ml of the appropriate refluxing solvent was used. The reaction times for preparation of the organometallic compound depended upon the particular experiment and are listed in the accompanying tables.

The alkyl halide (0.05 mole) was added to the cooled product (22°) slowly in order to avoid uncontrollable reaction. A 1-hour period of stirring at room temperature ensured complete reaction of the salt with the halide. The mixture was then poured into a separatory funnel containing water slightly acidified with dilute hydrochloric acid. The ether layer was separated and then dried over calcium chloride. After removal of the ether, a portion (1 g or less) of the product was passed through an 80 to 200 mesh alumina column, 60 cm × 1 cm, and eluted with pentane or hexane. Identification and estimation of the product in each small fraction (50 to 100 mg) was made by infrared spectroscopy using the absorption bands reported in Table II.

Crude benzylated fluorene was treated repeatedly with small portions of cold ethanol, thus effecting a separation of the soluble fluorene and monobenzylfluorene from the

sparingly soluble dibenzylated fluorene. Complete separation of fluorene from the monobenzylfluorene was not achieved.

Experiments using the metal amides instead of metals were carried out similarly using the same quantities of reagents.

Greenhow's method (2) for the preparation of 9-fluorenylsodium was not successful in our hands (1). Since the solid material was required in experiments, the reaction of sodium metal and fluorene in DME, DEE, and THF, although quite facile was of no assistance because the salt failed to precipitate. The reaction of equimolar quantities of fluorene and powdered sodamide in refluxing dioxane gave satisfactory results. From deuteration experiments (1) approximately two thirds of the fluorene had metalated when a mixture of 8.3 g of fluorene, 1.95 g of sodamide, and 25 ml of dioxane was refluxed for 4 hours. Longer reaction time increased the extent of metalation. The 9-fluorenylsodium was readily separated from dioxane, but unreacted sodamide was also retained as a contaminant which could not be removed. Hence, the results of all reactions with 9-fluorenylsodium prepared by this method must be considered with this in mind.

ACKNOWLEDGMENTS

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THE INTERACTION OF DISILOXANE WITH BORON TRIFLUORIDE AND TRICHLORIDE[1]

M. ONYSZCHUK

ABSTRACT

Disiloxane does not form stable adducts with boron trifluoride and trichloride, but cleavage of an Si—O bond occurs with formation of the corresponding monohalogenosilane and siloxyboron dihalide. Although siloxyboron dichloride is stable at room temperature, siloxyboron difluoride disproportionates into silyl fluoride, boron trifluoride, and boron trioxide. A stepwise mechanism involving four-center cyclic transition states is postulated for the over-all reaction.

Disilthian does not react with boron trifluoride. This indicates that the sulphur atom in the Si—S—Si linkage system has little, if any, electron-donor activity. The absence of electron-donor activity for oxygen and sulphur in Si—O—Si and Si—S—Si linkages is discussed.

In a previous paper (1) it was reported that boron trifluoride and trichloride do not form stable addition compounds with 1,1′-dimethyl-, 1,1′,2,2′-tetramethyl-, or hexamethyl-disiloxane: instead cleavage of an Si—O bond occurs with formation of the methylhalogenosilane and the methylsiloxyboron dihalide:

$$(CH_3SiH_2)_2O + BF_3 = CH_3SiH_2OBF_2 + CH_3SiH_2F.$$

The methylsiloxyboron dihalides are unstable at room temperature, decomposing into the methylhalogenosilane, boron trihalide, and boron trioxide:

$$3CH_3SiH_2OBF_2 = 3CH_3SiH_2F + BF_3 + B_2O_3.$$

Similarly, the interaction of hexamethyldisiloxane with aluminum chloride or bromide produces trimethylsiloxyaluminum dihalides, but these are much more stable than the boron analogues (2). However, the siloxyaluminum dihalides, SiH_3OAlX_2, which result from the reaction of disiloxane with aluminum halides, are non-volatile, presumably polymeric solids, which appear to react with silyl halide forming silylene halide, SiH_2X_2, and silane, especially when a large proportion of aluminum halide is used initially (3).

The experiments described in this paper were made to examine the interaction of disiloxane and disilthian with boron trifluoride and trichloride.

RESULTS AND DISCUSSION

It was not possible to confirm the formation of a 1:1 adduct between disiloxane and boron trifluoride when they were combined at −78°, since Si—O bond cleavage at this temperature produced silyl fluoride and siloxyboron difluoride:

$$(SiH_3)_2O + BF_3 = SiH_3F + SiH_3OBF_2. \qquad [1]$$

Siloxyboron difluoride, which was a white solid at −78°, decomposed gradually at higher temperatures into silyl fluoride, boron trifluoride, and boron trioxide, probably according to the equation:

$$3SiH_3OBF_2 = 3SiH_3F + BF_3 + B_2O_3. \qquad [2]$$

An infrared spectrum of the decomposition mixture (Fig. 1, Table I), however, suggested

[1]*Manuscript received December 16, 1960.*
Contribution from the University Chemical Laboratory, Cambridge, England, and the Inorganic Chemistry Laboratory, McGill University, Montreal 2, Que.

TABLE I

Infrared absorption bands for silyl halides and siloxyboron dihalides

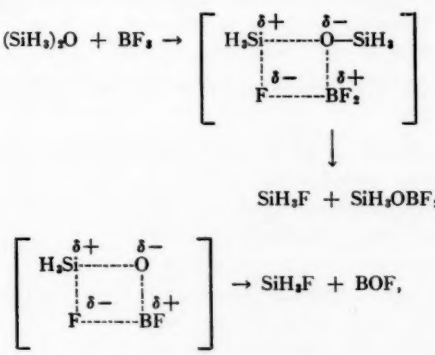
SiH_3F cm^{-1}	SiH_3OBF_2* cm^{-1}	SiH_3Cl cm^{-1}	SiH_3OBCl_2 cm^{-1}	Assignment
2225s 2210s	2200s	2215s 2195s	2210m	ν_{sym}(Si—H) and ν_{asym}(Si—H)
	1500m 1450vs			ν_{sym}(^{10}B—F) for BF_2 ν_{sym}(^{11}B—F) for BF_2
	1385m 1375m		1413m 1375s	ν(B—F) for —BF_2 and ν(B—O)
1100†vw	1105w	1100†vw	1100m	ν(Si—O)
1000vs	992s	952vs 940vs	996s 957vs	δ(Si—H)
			900m 885m	ν(B—Cl) for —BCl_2
874m 730m	875m 742m	675m	730w	ν(Si—F) for SiH_3F SiH_3 rock
	720m 692m			ν(^{11}B—F) for BF_2 ν(^{10}B—F) for BF_2

s = strong m = medium w = weak v = very

*Decomposition mixture.
†Due to disiloxane impurity.

the presence of siloxyboron difluoride in addition to silyl fluoride and boron trifluoride. Siloxyboron dichloride was much more stable than the difluoride, and a pure sample of the dichloride could be isolated so that its composition was confirmed by analysis.

These results show that cleavage of Si—O bonds in disiloxane by boron trihalides occurs in two stages, each of which probably involves a four-center cyclic transition state similar to those postulated for the interaction of boron trihalides with alkyl ethers (4), alkyldisiloxanes (5), and hexamethyldigermoxane (6). For example, the mechanism for the interaction of disiloxane with boron trifluoride can be represented as follows:



The initial step is thought to produce a 1:1 adduct which is stable only well below −78° and does not dissociate into the original reactants, but decomposes with cleavage of an Si—O bond presumably due to strong polar interactions in the four-center cyclic transition

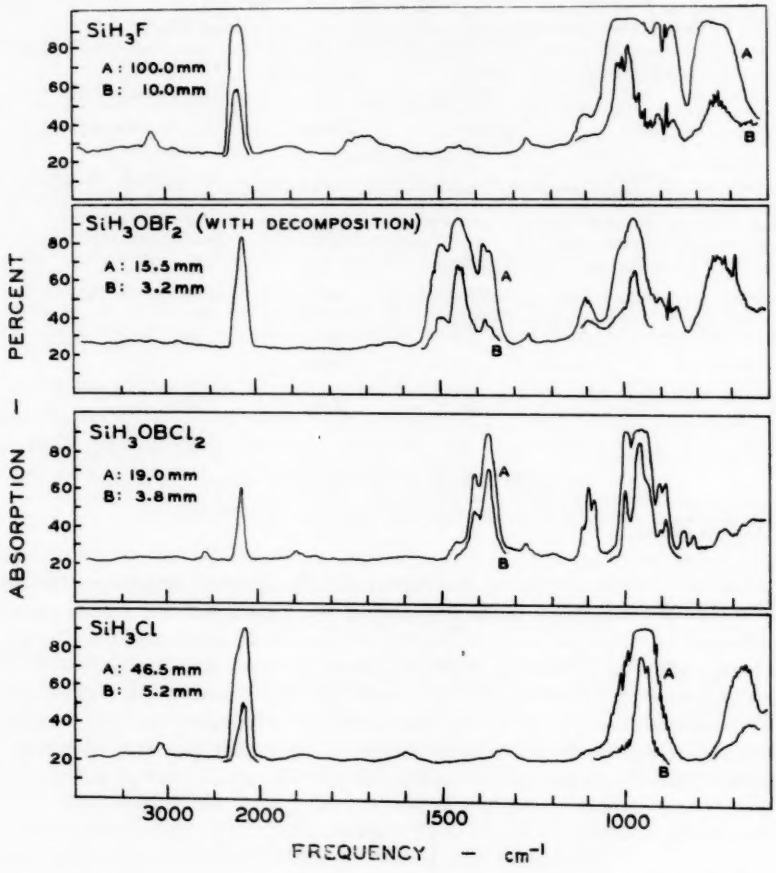


FIG. 1. A comparison of the infrared spectra of siloxyboron dihalides and silyl halides.

state. Probably the instability of siloxyboron difluoride also arises from intramolecular interaction between silicon and fluorine atoms, as indicated in the second step of the mechanism, although intermolecular disproportionation is equally probable. The higher thermal stability of siloxyboron dichloride compared with the difluoride might be attributed to weaker polar interaction between silicon and chlorine than that between silicon and fluorine, since chlorine is less electronegative than fluorine. The fact that boron oxyfluoride, resulting from the decomposition of siloxyboron difluoride, was not isolated is not surprising, because boron oxyfluoride exists as a cyclic trimer only below $-140°$ and disproportionates rapidly at higher temperatures into boron trifluoride and trioxide (7).

The over-all reaction of disiloxane with boron trifluoride at room temperature, which occurs almost quantitatively according to the following stoichiometric equation, provides a new convenient method for the preparation of silyl fluoride in high purity and yield:

$$3(SiH_3)_2O + 2BF_3 = 6SiH_3F + B_2O_3. \qquad [3]$$

Silyl fluoride was first prepared by Emeléus and Maddock (8) in 79% yield and in only 98% purity from the reaction of silyl chloride with antimony trifluoride. Sujishi and Witz (9) obtained tensiometrically pure silyl fluoride in good yield from the reaction of trisilylamine with boron trifluoride.

The failure of disiloxane to form stable adducts with boron trifluoride and trichloride does not necessarily indicate a complete lack of electron-donor activity of the oxygen atom in disiloxane, since Si—O bond cleavage probably concealed the initial formation of a 1:1 adduct. The electron-donor power of disiloxane cannot be high because d_π–p_π back co-ordination between silicon and oxygen atoms might greatly decrease the availability of the electron pairs at the oxygen atom for donation. This partial double bonding effect is thought to be the reason for the Si—O—Si bond angle being approximately 150° (10, 11), much larger than the tetrahedral angle expected if only σ bonding occurs between silicon and oxygen atoms. Since the Si—O—Si bond angle is definitely not 180°, it seems reasonable to suppose that the lone electron pairs on oxygen are not entirely back-bonded to silicon and therefore should still be available for donation, at least to a detectable degree. Co-ordination probably occurs between disiloxane and boron trifluoride or trichloride, but it is difficult to detect due to simultaneous Si—O bond cleavage. Similarly, iodine does not appear to form an oxonium complex with disiloxane, and only Si—O bond splitting is observed (12). Although Kriner, MacDiarmid, and Evers (3) observed a solid adduct when they combined disiloxane with dimethylaluminum bromide at −50°, the adduct did not dissociate at higher temperatures but decomposed instead, with cleavage of the Si—O—Si linkage. In order to determine precisely the degree of electron-donor activity of disiloxane, it will be necessary to examine its behavior with less polarizable acceptor molecules, which are less likely to cause Si—O bond rupture.

Since disilthian did not undergo any recognizable interaction with boron trifluoride, the sulphur atom in disilthian has little, if any, electron-donor activity. This conclusion is in complete agreement with the previous observation that disilthian does not form co-ordination compounds with silyl iodide, methyl iodide, iodine, mercuric iodide, or mercuric chloride (12). It has been suggested that d_π–p_π bonding between silicon and elements of groups V, VI, and VII is greater the more electronegative the donor atom (13). Accordingly, there should be less d_π–p_π bonding in the Si—S bond than in the Si—O bond, since sulphur is less electronegative than oxygen. This, together with the fact that the sulphur atom is larger than the oxygen atom, suggests that in silyl derivatives the lone electron pairs on sulphur should be more available for donation than those on oxygen. It is surprising, therefore, that disilthian does not form an adduct with boron trifluoride, one of the most powerful electron-acceptor molecules.

The infrared spectrum of the siloxyboron difluoride decomposition mixture (Fig. 1, Table I) shows absorption bands at 1385 and 1105 cm^{-1} in addition to those characteristic of silyl fluoride and boron trifluoride. The band at 1385 cm^{-1} undoubtedly includes the B—O stretching vibration, which occurs in the range 1350–1310 cm^{-1} in a large number of borates, boronates, and boronites (14). The 1385 cm^{-1} band probably also contains the B—F stretching mode of the $—BF_2$ group in SiH_3OBF_2 since this vibration is found at 1363 cm^{-1} in methyldifluoroborane (15). The band at 1105 cm^{-1} in the SiH_3OBF_2 decomposition mixture must be the Si—O stretching frequency in SiH_2OBF_2, because the same vibration occurs at 1106 cm^{-1} in disiloxane (12). These assignments are confirmed by comparison with the spectrum of SiH_3OBCl_2, which shows B—O and Si—O stretching frequencies at 1375 and 1100 cm^{-1} respectively. By analogy with the spectra of alkylphenylchloroboronites in which the B—Cl stretching mode is found between 909 and

893 cm^{-1}, the band with peaks at 900 and 885 cm^{-1} in the spectrum of SiH_3OBCl_2 is attributed to B—Cl stretching vibration of the $—BCl_2$ group. The spectra of SiH_3F and SiH_3Cl shown in Fig. 1 are essentially the same as those previously reported (16, 17, 18, 19), and they are included here for comparison with the spectra of SiH_3OBCl_2 and the SiH_3OBF_2 decomposition mixture.

EXPERIMENTAL

Apparatus and Methods

A glass high-vacuum apparatus of the conventional type with stopcocks lubricated with Apiezon L grease was used for the transfer, separation, and characterization of volatile substances. Prolonged contact of volatile substances with stopcock grease was avoided by using all-glass reaction vessels (100 ml) fitted with break seals, which could be opened magnetically.

Hydrogen bonded to silicon was determined by measurement of the hydrogen liberated after rapid hydrolysis with potassium hydroxide (30%) of an accurately weighed sample of the unknown. Halide ion in the hydrolyzate was estimated gravimetrically. Boron trioxide was determined by titration, to the phenolphthalein end point, of its aqueous solution with standard alkali in the presence of mannitol.

The infrared spectra of the compounds were recorded in the range 4000–650 cm^{-1} on a Perkin–Elmer model 21 double-beam spectrophotometer equipped with a rock-salt prism. The substances were examined in the vapor phase at measured pressures in a cylindrical cell of 5-cm diameter and 10-cm length fitted with 5-mm-thick sodium chloride end plates.

Materials

Samples of disilthian and silyl iodide were kindly provided by Dr. Allan G. MacDiarmid. Disiloxane was prepared by hydrolysis of silyl iodide and disilthian (12). Commercial grade boron trifluoride and trichloride were purified by fractional distillation in the vacuum apparatus. The purity of each substance was checked immediately before use by measurement of its vapor pressure and molecular weight (M).

Reaction of Disiloxane with Boron Trifluoride

When boron trifluoride (0.0581 g, 0.85 mmole) and disiloxane (0.1010 g, 1.28 mmole) were condensed together and kept at −78° for 12 hours, a white solid and a volatile substance were obtained. The latter was removed by distillation at −78° and then it was redistilled at −132°. The component volatile at −132° was silyl fluoride (0.0378 g, 1.44 mmole. Found: M, 51.2. Calc. for SiH_3F: M, 50.1), and the fraction not volatile at −132° but volatile at −78° was unreacted disiloxane (0.0139 g, 0.18 mmole. Found: M, 78.4. Calc. for $(SiH_3)_2O$: M, 78.0). The yield of silyl fluoride was 12% in excess of that calculated for reaction [1], and this additional silyl fluoride probably resulted from decomposition of some siloxyboron difluoride according to reaction [2].

The white solid product, which remained after removal of volatile products by distillation at −78°, decomposed gradually without melting when warmed to 25°. It gave a white non-volatile residue of boric oxide (0.0166 g) and a volatile fraction. The latter decomposed partially, during the measurement of its molecular weight at 25°, into boric oxide and a volatile component (0.0504 g, found: M, 72.4), which was thought to contain mainly siloxyboron difluoride (calc. M, 95.7) and lesser amounts of silyl fluoride (calc. M, 50.1) and boron trifluoride (calc. M, 67.8). Unfortunately this mixture decomposed

further with each trap-to-trap transfer, leaving white deposits of boric oxide in each trap and therefore a pure sample of siloxyboron difluoride could not be isolated. An infrared spectrum of the decomposition mixture (Fig. 1, Table I) confirmed the presence of silyl fluoride and boron trifluoride, and showed Si—O and B—O stretching bands which were attributed to siloxyboron difluoride.

The over-all yield of pure silyl fluoride (0.110 g, 2.18 mmole. Found: M, 50.4; v.p. 121.0 mm at −112°, lit. (9) v.p. 120.0 mm at −112.3°) was 85%, calculated on the amount of boron trifluoride used in the over-all reaction [3].

Reaction of Disiloxane with Boron Trichloride

After 12 hours at −78°, disiloxane (0.1001 g, 1.28 mmole) and boron trichloride (0.1507 g, 1.28 mmole) gave a colorless, transparent solid and a volatile substance. The latter was distilled at −96° and was found to be silyl chloride (0.1142 g, 1.71 mmole. Found: M, 66.9. Calc. for SiH_3Cl: M, 66.6). Since the yield of silyl chloride was 25% in excess of that calculated for the reaction: $(SiH_3)_2O+BCl_3 \rightarrow SiH_3Cl+SiH_3OBCl_2$, it was thought that the additional silyl chloride had been formed by decomposition of some siloxyboron dichloride. The substance which remained after the distillation at −96°, on distillation at −64°, gave a fraction (0.1167 g, found: M, 119; v.p. 24.0 mm at −45.5° and 55.7 mm at −27.5°) which contained mainly siloxyboron dichloride (calc. M, 128.8) and a small amount of silyl chloride (calc. M, 66.6). The residue was non-volatile white flaky boron trioxide (0.0101 g). A pure sample of siloxyboron dichloride was obtained after several distillations at −112° of the fraction with a molecular weight of 119 (0.0505 g, found: M, 130.0; H, as Si–H, 2.31%; Cl, 61.3%. Calc. for SiH_3OBCl_2: M, 128.8; H, as Si—H, 2.35%; Cl, 61.4%).

Attempted Reaction of Disilthian with Boron Trifluoride

There was no reaction between disilthian (0.1281 g, 1.34 mmole) and boron trifluoride (0.0916 g, 1.35 mmole) at −132°, −78°, or 20°, and in each case unchanged reactants were recovered quantitatively by distillation of the mixture at −132°. Because of this negative result, it did not seem practical to investigate the behavior of disilthian with boron trichloride.

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ENZYMIC HYDROLYSIS OF A GLUCOMANNAN FROM JACK PINE (PINUS BANKSIANA LAMB.)[1]

O. PERILA[2] AND C. T. BISHOP

ABSTRACT

A crude glucomannan was isolated from jack pine holocellulose in 17% yield. Repeated delignification and copper complexing of this product provided a purified glucomannan (5% of the holocellulose) containing glucose, mannose, galactose, and xylose in a molar ratio of 10:25:1:1. This polysaccharide was hydrolyzed by a commercial hemicellulase preparation, the cleavage products being removed by continuous dialysis of the reaction mixture. The following oligosaccharides were isolated from the hydrolyzate and identified; yields are based on the glucomannan:

(*a*)	4-*O*-(β-D-mannopyranosyl)-D-mannopyranose	18.5%,
(*b*)	4-*O*-(β-D-glucopyranosyl)-D-mannopyranose	1.4%,
(*c*)	4-*O*-(β-D-mannopyranosyl)-D-glucopyranose	0.7%,
(*d*)	6-*O*-(α-D-xylopyranosyl)-D-glucopyranose	0.5%,
(*e*)	*O*-β-D-mannopyranosyl (1 → 4)-*O*-β-D-mannopyranosyl (1 → 4)-D-mannopyranose	6.5%,
(*f*)	*O*-β-D-mannopyranosyl (1 → 4)-*O*-β-D-glucopyranosyl (1 → 4)-D-glucopyranose	0.7%,
(*g*)	*O*-α-D-xylopyranosyl (1 → 6)-*O*-β-D-glucopyranosyl (1 → 4)-D-glucopyranose	0.1%,
(*h*)	*O*-β-D-mannopyranosyl (1 → 4)-*O*-β-D-mannopyranosyl (1 → 4)-D-glucopyranose	0.04%,
(*i*)	*O*-β-D-glucopyranosyl (1 → 4)-*O*-β-D-mannopyranosyl (1 → 4)-D-mannopyranose	0.03%,
(*j*)	a trisaccharide containing arabinose, glucose, and mannose	0.01%,
(*k*)	a trisaccharide containing two units of arabinose and one of galactose	0.01%.

The constitutions of glucomannans from a variety of softwoods have been studied extensively during the past 10 years and much of this work has been summarized in a review by Aspinall (1). References to later work may be found in some of the more recent papers (2–5). All of these studies have shown that the glucomannans consist basically of β-D-mannose and β-D-glucose residues joined together in a chain by 1 → 4 linkages. Differences between the glucomannans from different woods occur in the presence or absence of small amounts of D-galactose which, when it occurs, has been found as terminal, non-reducing units. There is also some uncertainty about the presence of a slight degree of branching in the main chain of these polysaccharides.

Until recently, every one of the fully defined oligosaccharides obtained by partial acid hydrolysis of glucomannans was found to contain 1 → 4 linkages exclusively (4–10). However, Meier (3) has now reported the isolation of 6-*O*-α-D-galactopyranosyl-D-mannopyranose and this was the first unequivocal evidence of a linkage other than 1 → 4 in a glucomannan. Relative rates of acid hydrolysis of methyl glycopyranosides differ considerably (11) and it may be assumed that various linkages in a polysaccharide are also hydrolyzed at different rates. Oligosaccharides obtained by partial acid hydrolysis of polysaccharides will therefore contain primarily the most stable linkages. Relative rates of hydrolysis of glycosidic linkages by enzymes can be quite different from the rates of hydrolysis by acids because the former are more specific catalysts. Oligosaccharides obtained by enzymic hydrolysis can therefore differ considerably from those obtained by acid hydrolysis of the same polysaccharide and an examination of such products can

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yield new information about the linkages in the polymer. It is also possible to obtain higher yields of oligosaccharides through enzymic hydrolysis than acid hydrolysis by using dialysis for continuous removal of partly hydrolyzed fragments before they are degraded further (12).

A previous publication (2) described the gross structural features of a glucomannan from jack pine: this paper reports the isolation and identification of some of the oligosaccharides obtained by enzymic hydrolysis of that polysaccharide.

The crude polysaccharide was obtained in 17% yield from jack pine holocellulose prepared by the chlorine–monoethanolamine method (13). The crude product was purified by alternate delignification and precipitation as its copper complex, this cycle being repeated three times. The resulting polysaccharide (5% of the holocellulose) contained glucose, mannose, galactose, and xylose in a molar ratio of 10:25:1:1. Further precipitations as the copper complex gave products with a lower xylose content but recoveries fell off so sharply that it was difficult to decide whether this was removal of a xylan or simply fractionation of glucomannan molecules to which were attached small and varying amounts of galactose and xylose units. Croon, Lindberg, and Meier (14) have reported that a glucomannan from Scots pine could be freed from galactose- and xylose-containing impurities after further delignification. They believed that different polysaccharides were joined to the same lignin molecule thus preventing their separation prior to delignification. It is unlikely that this could explain the presence of galactose and xylose in the glucomannan used in the present study because the product was delignified three times after its isolation from the holocellulose. The glucomannan isolated from jack pine in the present work differed from that used in the previous study (2) in containing xylose; the molar ratios of the other three monosaccharides were in good agreement. This difference could conceivably be attributed to the two different methods of delignification. Acid chlorite (15) is known to degrade polysaccharides (16) and its use for delignification in the earlier work may have caused hydrolysis of the xylose units. The chlorine–monoethanolamine method (13) causes little degradation (16) and was used here specifically to preserve labile linkages which might then be detected in the products from enzymic hydrolysis.

The enzyme used was a commercially available hemicellulase which undoubtedly contained a variety of enzymes. However, it was lacking in cellulase activity and did not attack the cellophane tubing used for dialysis. Hydrolyses were carried out in dialysis tubing, a technique first developed by Painter (12). The apparatus used in the present work (Fig. 1) permitted stirring of the hydrolysis mixture and continuous removal of the dialyzable products. A purified cellulase (17) did not yield any dialyzable products from the glucomannan and a commercial pectinase yielded only monosaccharides.

Yields of products from hemicellulase hydrolysis of jack pine glucomannan are given in Table I. A mixture of higher oligosaccharides (8.2% of the glucomannan) was also recovered but was not examined further.

The following methods were used, where necessary, to establish identities of the oligosaccharides: total hydrolysis followed by paper chromatography revealed the component monosaccharides; reduction with potassium borohydride (18) followed by hydrolysis and paper chromatography showed which monosaccharide formed the reducing end groups; oxidation by lead tetraacetate and by periodate (19, 20), followed in some cases by reduction, hydrolysis, and paper chromatography (20–22), gave information about specific linkages; partial hydrolysis of trisaccharides yielded disaccharides which were identified by paper chromatography and provided further evidence for the location of linkages; anomeric configurations were based on specific rotations and, for some of the

TABLE I

Products from enzymic hydrolysis of jack pine glucomannan

Monosaccharides (39.9%)	
D-Glucose	14.7%
D-Mannose	21.8%
D-Galactose	2.1%
D-Xylose	1.6%
Disaccharides (20.9%)	
(*a*) 4-*O*-(β-D-Mannopyranosyl)-D-mannopyranose	18.5%
(*b*) 4-*O*-(β-D-Glucopyranosyl)-D-mannopyranose	1.4%
(*c*) 4-*O*-(β-D-Mannopyranosyl)-D-glucopyranose	0.7%
(*d*) 6-*O*-(α-D-Xylopyranosyl)-D-glucopyranose	0.5%
Trisaccharides (7.6%)	
(*e*) *O*-β-D-Mannopyranosyl(1 → 4)-*O*-β-D-mannopyranosyl(1 → 4)-D-mannopyranose	6.5%
(*f*) *O*-β-D-Mannopyranosyl(1 → 4)-*O*-β-D-glucopyranosyl(1 → 4)-D-glucopyranose	0.7%
(*g*) *O*-α-D-Xylopyranosyl(1 → 6)-*O*-β-D-glucopyranosyl(1 → 4)-D-glucopyranose	0.1%
(*h*) *O*-β-D-Mannopyranosyl(1 → 4)-*O*-β-D-mannopyranosyl(1 → 4)-D-glucopyranose	0.04%
(*i*) *O*-β-D-Glucopyranosyl(1 → 4)-*O*-β-D-mannopyranosyl(1 → 4)-D-mannopyranose	0.03%
(*j*) A trisaccharide containing arabinose, glucose, and mannose	0.01%
(*k*) A trisaccharide containing two units of arabinose and one of galactose	0.01%

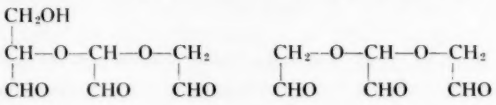
trisaccharides, were inferred from the identities of products of partial hydrolysis with disaccharides of known configuration; methylation and methanolysis yielded methyl-*O*-methyl glycosides which were identified and estimated by gas–liquid partition chromatography (23, 24) giving qualitative and quantitative data on the specific linkages. The latter method was used on a microscale (0.5–2.0 mg) after it was found that methylation by the Kuhn (25) procedure did not require protection of the reducing groups by prior glycosidation. Neither D-glucose or cellobiose, when methylated by this procedure, yielded any acidic products which would have resulted from oxidation of the reducing group by silver oxide. Furthermore, the fully methylated cellobiose yielded equimolar amounts of 2,3,4,6-tetra-*O*-methyl- and 2,3,6-tri-*O*-methyl-D-glucose on methanolysis proving that no oxidation of the reducing group had occurred.

Oligosaccharide (*a*) was isolated in crystalline form having the same physical constants as an authentic sample of 4-*O*-(β-D-mannopyranosyl)-D-mannopyranose. In addition to the crystalline anhydrous product a crystalline monohydrate (m.p. 122–124° C) was isolated which does not appear to have been reported previously.

Oligosaccharide (*b*) was also obtained as crystals and had the same physical constants as an authentic sample of 4-*O*-(β-D-glucopyranosyl)-D-mannopyranose. Hydrolysis of the oligosaccharide yielded equal amounts of glucose and mannose while hydrolysis after reduction yielded glucose as the only reducing monosaccharide.

Oligosaccharide (*c*) was obtained as an amorphous product having a specific rotation within the range reported for 4-*O*-(β-D-mannopyranosyl)-D-glucopyranose. The compound was chromatographically pure in five different solvent systems and showed the same rates of movement as an authentic sample of this disaccharide. Hydrolysis yielded equimolar amounts of glucose and mannose; reduction and hydrolysis yielded mannose as the only monosaccharide. Oxidation with lead tetraacetate gave 1.3 moles of carbon dioxide per mole disaccharide with consumption of 3.7 moles of oxidant; calculated values are 1.0 and 4.0 moles/mole respectively. Reduction and hydrolysis of the oxidized product yielded erythritol and glycerol in approximately equal amounts. Methylation and methanolysis of the disaccharide yielded methyl glycosides of 2,3,4,6-tetra-*O*-methyl-D-mannose and 2,3,6-tri-*O*-methyl-D-glucose; the molar ratio of these *O*-methyl ethers was 1:1. Oligosaccharide (*c*) was therefore 4-*O*-(β-D-mannopyranosyl)-D-glucopyranose.

Oligosaccharide (*d*) was an amorphous product, chromatographically pure in three different solvent systems. Hydrolysis yielded equal amounts of xylose and glucose; hydrolysis of the reduced disaccharide yielded xylose as the only reducing sugar. Methylation and methanolysis of the disaccharide yielded glycosides of 2,3,4-tri-*O*-methyl-D-xylose and 2,3,4-tri-*O*-methyl-D-glucose, the two compounds being present in a molar ratio of 1:1. This evidence together with the high positive rotation ($[\alpha]_D+70°$) showed that oligosaccharide (*d*) was 6-*O*-(α-D-xylopyranosyl)-D-glucopyranose. Zemplen and Bognar (26) have reported the synthesis of this compound and obtained it in crystalline form, m.p. 200.5–201.5° C, $[\alpha]_D^{20}+150 \rightarrow 121°$ (16 hours in water). The assigned structure for oligosaccharide (*d*) is supported by the fact that when the compound was treated with lead tetraacetate in the presence of potassium acetate, 4.8 moles of oxidant were consumed per mole and 3.5 moles of carbon dioxide were evolved per mole, without the production of formaldehyde. These data eliminate any likelihood that the D-glucose reducing end unit was substituted at position 2, 3, or 4, and correspond to those expected for a $1 \rightarrow 6$ linked xylopyranosyl-glucose containing about 20% of non-oxidizable impurity.* The fact that the compound was extremely hygrosopic may account for the



I II

low oxidation, as well as rotational values.

Oligosaccharide (*e*) was obtained in two crystalline forms having melting points of 166–167° C and 214–216° C. Whistler and Smith (27) have reported the trihydrate of mannotriose as having a melting point of 137–137.5° C. Aspinall *et al.* (28) obtained the same melting point with rapid heating of the sample but noted that slow heating gave a melting point of 166.5–169.5° C and presumed that this was the anhydrous form of the trisaccharide. The lower melting form of oligosaccharide (*e*) did not depress the melting point of an authentic sample of *O*-β-D-mannopyranosyl $(1 \rightarrow 4)$-*O*-β-D-mannopyranosyl $(1 \rightarrow 4)$-D-mannopyranose having a melting point of 166–167° C. Elementary analysis showed that this compound was the monohydrate of the trisaccharide. Recrystallization of this product from hot, absolute ethanol yielded a crystalline compound with a melting point of 214–216° C. Analysis showed that this was the anhydrous form of mannotriose which does not appear to have been reported previously. It is apparent that the $1 \rightarrow 4$-β-linked mannotriose can be isolated as the trihydrate (m.p. 137–137.5° C), the monohydrate (m.p. 166–169° C), or the anhydrous sugar (m.p. 214–215° C). The specific rotation of oligosaccharide (*e*) was within the range of those reported for *O*-β-D-mannopyranosyl$(1 \rightarrow 4)$-*O*-β-D-mannopyranosyl$(1 \rightarrow 4)$-D-mannopyranose and methylation and methanolysis yielded glycosides of 2,3,4,6-tetra-*O*-methyl-D-mannose and 2,3,6-tri-*O*-methyl-D-mannose in a molar ratio of 1:2.

Oligosaccharide (*f*) was an amorphous product, chromatographically pure in five different solvent systems, and yielding on hydrolysis mannose and glucose in a molar

Other structures not inconsistent with these oxidation data are 6-O-(D-xylofuranosyl)-D-glucose and 5-O-(D-xylopyranosyl)-D-glucose. When oxidized by periodate such compounds should yield trialdehyde I (free aldehyde form) having $[\alpha]_D \pm 85°$ to 100° (the sign and value depending on the stereochemistry); however, 6-O-(D-xylopyranosyl)-D-glucose should yield optically inactive trialdehyde II (A. J. Charlson and A. S. Perlin. Can. J. Chem. **34, 1804 (1956)). When oligosaccharide (d) was oxidized with excess periodate the rotation dropped rapidly to a constant value of zero, evidence for formation of II (A. S. Perlin. Private communication).*

ratio of 1:2. The hydrolyzate of the reduced trisaccharide contained mannose and glucose in a molar ratio of 1:1 showing that the reducing end group in the trisaccharide was a glucose unit. Partial hydrolysis yielded glucose, mannose, and two disaccharides that were chromatographically identical with cellobiose and 4-*O*-(β-D-mannopyranosyl)-D-glucopyranose. Lead tetraacetate oxidation of the trisaccharide yielded 1.0 mole of formic acid and oxidant consumption was 3.7 moles. Assuming oxidation of a pyranosyl non-reducing end and a C_4-substituted reducing end the required values are 1.0 mole of formic acid and 4.0 moles of oxidant consumed. It has been shown that 2,3-trans glycols on the central residues of $1 \rightarrow 4$ linked trisaccharides are not oxidized by lead tetraacetate (29). Reduction and hydrolysis of the oxidation product from oligosaccharide (*f*) yielded glycerol, erythritol, and glucose which arose from the non-reducing unit, the C_4-substituted reducing group, and the central unit respectively of the trisaccharide. Methylation and methanolysis yielded glycosides of 2,3,4,6-tetra-*O*-methyl-D-mannose and 2,3,6-tri-*O*-methyl-D-glucose which were present in a ratio of 1:2. The foregoing results established that oligosaccharide (*f*) was *O*-β-D-mannopyranosyl$(1 \rightarrow 4)$-*O*-β-D-glucopyranosyl $(1 \rightarrow 4)$-D-glucopyranose.

Oligosaccharide (*g*) was isolated as an amorphous product, chromatographically pure in four different solvent systems. A sample crystallized after being kept for several weeks but was too small to permit recrystallization; melting point of the crude product was 147–150° C. Hydrolysis of oligosaccharide (*g*) yielded xylose and glucose in a molar ratio of 1:2 and hydrolysis of the reduced trisaccharide yielded xylose and glucose in a ratio of 1:1. Methylation and methanolysis yielded equimolar amounts of methyl glycosides of 2,3,4-tri-*O*-methyl-D-xylose; 2,3,4-tri-*O*-methyl-D-glucose; and 2,3,6-tri-*O*-methyl-D-glucose. The 2,3,6-tri-*O*-methyl-D-glucose was not present after methylation and methanolysis of the reduced trisaccharide. These results indicated that oligosaccharide (*g*) was *O*-α-D-xylopyranosyl$(1 \rightarrow 6)$-*O*-β-D-glucopyranosyl$(1 \rightarrow 4)$-D-glucopyranose. The anomeric configurations were assumed to be the same as in the other oligosaccharides where these linkages were found; i.e., the xylosyl–glucose $(1 \rightarrow 6)$ linkage was α in oligosaccharide (*d*) because of the high positive rotation and the glucosyl–glucose $(1 \rightarrow 4)$ linkage was β in oligosaccharide (*f*) because cellobiose was obtained on partial hydrolysis.

Oligosaccharide (*h*) was isolated in quantities too small for completely unequivocal identification. Hydrolysis yielded mannose and glucose with the former predominating. Hydrolysis after reduction yielded only mannose. Methylation and methanolysis gave methyl glycosides of 2,3,4,6-tetra-*O*-methyl-D-mannose; 2,3,6-tri-*O*-methyl-D-mannose; and 2,3,6-tri-*O*-methyl-D-glucose. Assuming the anomeric configurations and ring forms to be the same as found previously for these units it appeared that the oligosaccharide was *O*-β-D-mannopyranosyl $(1 \rightarrow 4)$-*O*-β-D-mannopyranosyl $(1 \rightarrow 4)$-D-glucopyranose.

Oligosaccharide (*i*) was also obtained in only small amounts. Hydrolysis yielded mannose and glucose with the former predominating. Methylation and methanolysis yielded glycosides of 2,3,4,6-tetra-*O*-methyl-D-glucose and 2,3,6-tri-*O*-methyl-D-mannose in a molar ratio of 1:2. Making the same assumptions as above this oligosaccharide was *O*-β-D-glucopyranosyl $(1 \rightarrow 4)$-*O*-β-D-mannopyranosyl $(1 \rightarrow 4)$-D-mannopyranose.

Oligosaccharide (*j*) yielded approximately equal amounts of arabinose, glucose, and mannose on hydrolysis and oligosaccharide (*k*) yielded galactose and arabinose in a ratio of 1:2. Both of these oligosaccharides were obtained in quantities too small for further investigation.

With a few notable exceptions the results of enzymic hydrolysis were similar to those

obtained by partial acid hydrolysis of glucomannans. The major products, mannobiose and mannotriose (oligosaccharides *a* and *e*) were obtained in a total yield of 25% from the glucomannan and showed the presence of extensive chains of $1 \rightarrow 4$ linked β-D-mannopyranose units. The significance of the relative amounts of oligosaccharides containing more than one monosaccharide is rather difficult to assess because the enzyme system used for hydrolysis contained enzymes of unknown specificities and reactivities. Oligosaccharides (*b*), (*c*), (*f*), (*h*), and (*i*) each contained β-D-glucose and β-D-mannose units joined by $1 \rightarrow 4$ linkages in various combinations. These results support the premise that the backbone of glucomannans is linear and confirm results found by partial acid hydrolysis (3–10); they also confirm the results of periodate oxidation of the glucomannan from jack pine which showed that there was no branching through C_2 or C_3 of any of the units (2). No cellobiose was found among the disaccharides but two trisaccharides (*f* and *g*) were obtained in which two glucose residues were joined together. The yield of trisaccharide (*f*) was of the same order as the other products of hydrolysis with exception of mannobiose and mannotriose, and indicated that some of the glucose residues in the polysaccharide were present in blocks of two or more units. The enzymic hydrolysis must have enriched these components because the enzyme used did not have any cellulase activity and a purified cellulase (17) of known specificity did not yield any dialyzable products from the polysaccharide.

The significance of oligosaccharides (*j*) and (*k*) is doubtful because the quantities were so small that polysaccharide impurities from the paper chromatograms (30) could contribute to the hydrolysis products.

To our knowledge oligosaccharides (*d*) and (*g*) represent the first evidence of a linkage between xylose and glucose units in wood polysaccharides. It was unlikely that these two oligosaccharides were products of enzymic synthesis or transfer reactions because the yields were as high or higher than other oligosaccharides which contained the $1 \rightarrow 4$ linkage. Also, no oligosaccharides were formed from monosaccharides that were incubated with the enzyme mixture under the same conditions used for the hydrolysis. The possibility seems remote that "transferases", if present, would transfer only xylose units and with glucose as the exclusive acceptor. It would therefore appear that oligosaccharides (*d*) and (*g*) were real hydrolysis products of a polysaccharide, either a xyloglucan or a xyloglucomannan, the presence of which has not been suspected before. A number of publications dealing with glucomannans have reported the presence of xylose in the polysaccharide, the amounts ranging from trace amounts to 3.0% (3, 4, 7–10, 14). This xylose has been ascribed to the presence of small amounts of acidic xylans which occur in those woods and which were not removed completely by the fractionation procedures used. The present work indicates that at least some of the xylose units in these preparations may have been attached to a glucose-containing polysaccharide and this could explain the failure to remove them completely by fractionation. Neither a pure mannan or a pure glucan (other than cellulose) has ever been isolated from wood; the evidence available at the present time indicates that glucomannans in the native state exist as linear molecules composed of glucose and mannose residues and containing small and varying amounts of xylose and galactose units as short side chains. This situation is remarkably similar to the xylans where small and varying amounts of 4-*O*-methyl-D-glucuronic acid and L-arabinose are attached to linear xylan molecules. The separation of "pure" polysaccharides from such mixtures, e.g. a glucomannan from a glucomannan containing 2–3% galactose or xylose, is extremely difficult by present methods.

EXPERIMENTAL

Paper chromatograms were run at room temperature (25°±2° C) by the descending method on Whatman No. 1 paper using the following solvent systems (v/v):

(A) butan-1-ol:pyridine:water—6:4:3; 2–3 days for di- and 4–6 days for tri-saccharides;

(B) butan-1-ol:pyridine:benzene:water—5:3:1:3; organic phase, 3–5 days for di- and 6–10 days for tri-saccharides;

(C) propan-1-ol:ethyl acetate:water—7:1:2; 3–5 days for di- and 6–10 days for tri-saccharides;

(D) ethyl acetate:pyridine:water—5:2:5; organic phase, 2–3 days for di- and 4–6 days for tri-saccharides;

(E) ethyl acetate:acetic acid:water—3:1:3; organic phase, 1–2 days for monosaccharides;

(F) ethyl acetate:pyridine:water—8:2:1; 1–2 days for monosaccharides;

(G) ethyl acetate:acetic acid:water—9:2:2; 5–10 days for di- and 10–20 days for tri-saccharides.

Sugars on the chromatograms were detected by aniline hydrogen phthalate (31) or *p*-anisidine hydrochloride (32) spray reagents or by successive dipping in methanolic silver nitrate, ethanolic sodium hydroxide, and aqueous sodium thiosulphate (33). The R_c values cited are migrations of sugars relative to that of cellobiose.

Evaporations were carried out under reduced pressure at 35° C, specific rotations are equilibrium values unless stated otherwise, and melting points are corrected.

Isolation of Glucomannan

Extractive-free jack pine wood was delignified by the chlorine–monoethanolamine procedure to yield holocellulose amounting to 63% of the extractive-free wood. The holocellulose (100 g) was extracted by stirring with 4% aqueous sodium hydroxide (1500 ml) in an atmosphere of nitrogen at 25° C for 24 hours. The residue was filtered and washed with 4% aqueous sodium hydroxide (1500 ml). The extract and washings were discarded. The residue was then extracted with alkaline borate solution (1500 ml) containing 17.5% sodium hydroxide and 4% boric acid (34) under the same conditions used before. The mixture was cooled in ice, filtered, and the residue was washed rapidly with cold, distilled water (1500 ml). Addition of freshly prepared Fehling's solution (250 ml) to the combined extract and washings caused precipitation of a polysaccharide copper complex (35). The precipitate was centrifuged and washed, twice with alkaline borate containing a small amount of Fehling's solution; twice with water containing a small amount of Fehling's solution; and finally twice with water. The copper complex was then dissolved in an ice-cold solution of *N* acetic acid and *N* hydrochloric acid (1:1). The clear solution was poured into an equal volume of ethanol and the precipitated polysaccharide was washed twice with ethanol and twice with water. Yield, determined on an aliquot of the aqueous suspension, was 17% of the holocellulose.

Purification of Glucomannan

Fresh chlorine water (10 g chlorine per liter) was added to the aqueous suspension of the crude glucomannan and the mixture was stirred thoroughly for 5 minutes. Hot 3% ethanolic monoethanolamine was added and the glucomannan was recovered by centrifugation. The precipitate was washed twice with the hot ethanolic monoethanolamine, twice with ethanol, twice with water and dissolved again in alkaline borate from which

it was precipitated as its copper complex by addition of Fehling's solution. The copper complex was washed and the glucomannan was recovered exactly as described above. The delignification and copper complexing were repeated two more times to yield a purified glucomannan, 5% of the holocellulose.

This polysaccharide had $[\alpha]_D^{26} = -25°$ (C, 1.2% in *N* sodium hydroxide) and upon hydrolysis by 30% formic acid in a sealed tube at 97° C for 15 hours yielded glucose, mannose, galactose, and xylose in a molar ratio of 10:25:1:1. The monosaccharides were separated chromatographically in solvent F and were estimated by the colorimetric procedure of Perila and Seppa (36).

Enzymic Hydrolysis of Glucomannan

The glucomannan was suspended in water at a concentration of 1–2% and dialyzed against distilled water through cellophane tubing for 24 hours. Hemicellulase (Nutritional Biochemicals Corporation) was added (10% of the dry weight of glucomannan) and the dialysis tube, closed at one end, was inserted into the large tube (A) of the dialysis apparatus (Fig. 1). The stirrer (B) was placed inside the dialysis tubing, the top of which was then fastened to the stirrer bearing (C), which was clamped in a fixed position. The

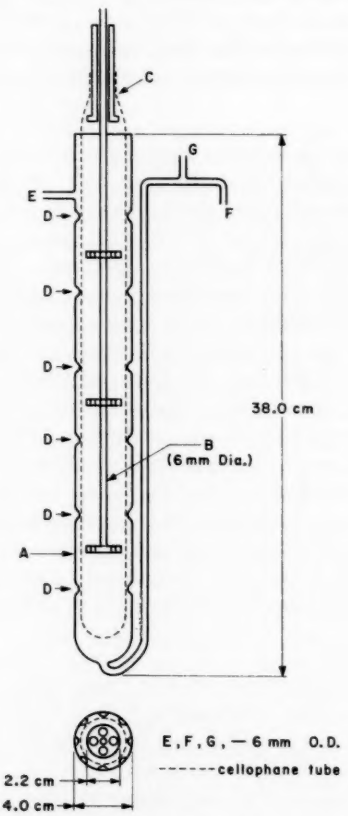


FIG. 1. Apparatus for continuous dialysis of enzymic hydrolyzates of polysaccharides.

stirrer was fastened to a concentric cam mounted on a stirring motor and of such size that the amplitude of the vertical movement of the stirrer was within the distance between the rings of indentations (D). The indentations served to hold the dialysis tubing away from the walls and permitted the passage of water around the entire surface. Water was introduced at E and collected at F at a rate of 1–2 ml per minute; the opening G prevented siphoning. Hydrolyses were carried out at 35° C, pH 6 without buffer, and were stopped when there was a drop in osmotic pressure within the dialysis tubing (100 hours). The dialyzate was evaporated and dried over anhydrous calcium chloride at 0.03 mm pressure. The yield of dialyzable products was 95±2% of the glucomannan.

Isolation of Oligosaccharides

The mixture of dialyzable products was chromatographed on a column of charcoal: Celite (37) using gradient elution (38) with water to 50% ethanol. The 500 fractions that were collected were examined by paper chromatography (solvent D) and similar fractions were combined to give 15 different fractions. Individual components were isolated from these fractions by chromatography on cellulose columns using butan-1-ol nearly saturated with water and by chromatography on large sheets of Whatman No. 3MM paper using solvents D and C. The isolated oligosaccharides were deionized by Amberlite IR-120 and IR-45, filtered through charcoal, and extracted with ether to remove any oils, fats, or waxes.

Hydrolysis of Oligosaccharides

Samples (ca. 0.5 mg) were heated in sealed tubes with 0.3 *N* hydrochloric acid at 97° C for 4 hours. Hydrolyzates were examined by paper chromatography using solvent E.

Reduction of Oligosaccharides

The oligosaccharide (1–2 mg) in water (0.5 ml) was added slowly to a solution of potassium borohydride (0.05 g) in water (1 ml) and the reaction was kept at room temperature for 18 hours. Amberlite IR-120 ion exchange resin was added until gas evolution ceased. The resin was filtered off, the filtrate was evaporated to dryness, and the residue was evaporated to dryness three times from methanol solution.

Methylation of Oligosaccharides

The oligosaccharide (0.5–2.0 mg) was shaken with methyl iodide (0.2 ml), dimethylformamide (0.2 ml), and silver oxide (0.2 g) at room temperature in the dark for 18 hours (25). The mixture was filtered and the residue was washed with chloroform. The combined filtrate and washings were dried (anhydrous calcium sulphate) and evaporated to dryness under 0.03 mm pressure at room temperature. The methylated oligosaccharides were refluxed in 2% methanolic hydrogen chloride for 20 hours and the resulting methyl glycosides were analyzed by gas–liquid partition chromatography (24). Separations were carried out using the following columns:

(*a*) 10% by weight of methylated hydroxyethylcellulose (39) on acid-washed Celite, 60–80 mesh, at 150° C and 180° C;

(*b*) 10% by weight of butanediol succinate polyester on Chromosorb W, 60–80 mesh, at 150° C;

(*c*) 10% by weight of Apiezon M on alkali-washed Celite, 60–80 mesh, at 150° C;

(*d*) 15% by weight of polyphenyl ether, *m*-bis(*m*-phenoxy-phenoxy)-benzene, on Celite, at 150° C.

The instrument used was a Pye Argon Chromatograph and gas flow rates were ca. 200 ml/min for columns (*a*), (*b*), and (*c*), ca. 100 ml/min for column (*d*). The methyl

O-methyl glycosides were identified by comparing their retention volumes with those of authentic samples run under the same conditions. The gas–liquid chromatographic behavior of most of the compounds found had been established previously by their isolation from the effluent gas stream (2, 23, 24, 40).

Oxidation of Oligosaccharides

Dr. A. S. Perlin kindly carried out the lead tetraacetate and periodate oxidations on 5–10 mg samples according to methods described previously by him and his colleagues (19, 20, 29).

Monosaccharides

Monosaccharides in the enzymic hydrolyzate were separated from the aqueous eluate of the charcoal column by paper chromatography in solvent E. Estimation (36) of the component sugars gave glucose, mannose, galactose, and xylose in a molar ratio of 10:15:1:1 respectively.

Oligosaccharides

M = mannopyranose; G = glucopyranose; X = xylopyranose.

Oligosaccharide (a) (M1 $\xrightarrow{\beta}$ 4M)

This component was eluted from the charcoal column by 0–5% ethanol. It was chromatographically identical with 4-*O*-(β-D-mannopyranosyl)-D-mannopyranose and had the following R_c values: solvent A, 1.0; B, 1.1; C, 1.2; D, 1.0; and G, 1.25. Crystallized from ethanol containing a little water the compound had a melting point of 122–124° C. Anal. Calc. for $C_{12}H_{22}O_{11}.H_2O$: C, 40.00%; H, 6.72%. Found: C, 40.32%; H, 6.82%. Crystallized from cold methanol the compound had a melting point of 190–191° C, undepressed by admixture with authentic mannobiose, $[\alpha]_D^{25} = -8.5°$ (*c*, 1.3% in water). Reported values are melting points within the range 193–210° C (4, 5, 8–10, 27, 28) and specific rotations from −5° to −9° (4, 5, 8–10, 28).

Oligosaccharide (b) (G1 $\xrightarrow{\beta}$ 4M)

This component was eluted from charcoal by 5–10% ethanol and was chromatographically identical with an authentic sample of 4-*O*-(β-D-glucopyranosyl)-D-mannopyranose. R_c values in different solvents were: A, 1.15; B, 1.25; C, 1.3; D, 1.2; and G, 1.6. Crystallized from methanol it had a melting point and mixed melting point of 133–135° C, $[\alpha]_D^{25} = +5.5°$ (*c*, 1.9% in water). Reported values (4, 5, 8–10) are for melting points within the range 133–139° C and specific rotations from +5° to +16°.

Oligosaccharide (c) (M1 $\xrightarrow{\beta}$ 4G)

This compound was eluted from charcoal by 0–5% ethanol and was chromatographically identical with an authentic sample of 4-*O*-(β-D-mannopyranosyl)-D-glucopyranose. R_c values in different solvents were: A, 0.8; B, 0.85; C, 0.75; D, 0.7; and G, 0.85. The product could not be crystallized and had $[\alpha]_D^{25} = +12°$ (*c*, 1.0% in water). Reported values range from +5° to +29° (4–10).

Oligosaccharide (d) (X1 $\xrightarrow{\alpha}$ 6G)

This compound was eluted from charcoal by 5–10% ethanol and had the following R_c values in different solvents: A, 1.1; B, 1.15; C, 1.25. The product was extremely hygroscopic but a specific rotation on the crude material showed $[\alpha]_D^{25} = +70°$ (*c*, 0.7% (?) in water; reported (26) for 6-*O*-(α-D-xylopyranosyl)-D-glucopyranose, $[\alpha]_D^{20} = +150° \rightarrow 121°$ (16 hours in water).

Oligosaccharide (e) (M1 $\xrightarrow{\beta}$ 4 M1 $\xrightarrow{\beta}$ 4M)

This compound was contained in the 5% ethanol eluate from the charcoal column and was chromatographically identical with an authentic sample of *O*-β-D-mannopyranosyl (1 → 4)-*O*-β-D-mannopyranosyl (1 → 4)-D-mannopyranose. R_e values in different solvents were: A, 0.5; B, 0.45; C, 0.5; D, 0.45; and G, 0.3. Crystallized from cold ethanol containing a small amount of water the product had m.p. 166–167° C undepressed by admixture with an authentic specimen. Reported melting points range between 155 and 169° C (4, 5, 8, 10, 28).

Anal. Calc. for $C_{18}H_{32}O_{16}.H_2O$: C, 41.39%; H, 6.58%. Found: C, 41.35%; H, 6.72%. Crystallized from hot ethanol the compound had a melting point of 214–216° C.

Anal. Calc. for $C_{18}H_{32}O_{16}$: C, 42.86%; H, 6.39%. Found: C, 42.71%; H, 6.38%. Specific rotation, calculated for the anhydrous compound, was the same for both forms: $[\alpha]_D^{25} = -23°$ (*c*, 2% in water); reported values range from −15° to −26° (4, 5, 8–10, 27, 28).

Oligosaccharide (f) (M1 $\xrightarrow{\beta}$ 4 G1 $\xrightarrow{\beta}$ 4G)

This component was eluted from the charcoal column by 15% ethanol and had the following R_e values in different solvents: A, 0.4; B, 0.35; C, 0.3; D, 0.25; and G, 0.25. Partial hydrolysis was done with 0.03 *N* oxalic acid for 10 hours at 97° C in a sealed tube. The amorphous compound had $[\alpha]_D^{28} = +9.5°$ (*c*, 1% in water).

Oligosaccharide (g) (X1 $\xrightarrow{\alpha}$ 6 G1 $\xrightarrow{\beta}$ 4G)

This compound was eluted from the charcoal column by 20% ethanol and had the following R_e values in different solvents: A, 0.8; B, 0.7; C, 0.75; and D, 0.5. A small sample crystallized after being kept for several weeks; melting point of the crude product was 147–150° C, $[\alpha]_D^{24} = +150°$ (*c*, 0.2% in water).

Oligosaccharide (h) (M1 $\xrightarrow{\beta}$ 4 M1 $\xrightarrow{\beta}$ 4G)

This compound was contained in the 10% ethanol eluate from the charcoal column and had R_e 0.8 in solvent C.

Oligosaccharide (i) (G1 $\xrightarrow{\beta}$ 4 M1 $\xrightarrow{\beta}$ 4M)

This compound was also in the 10% ethanol eluate and had R_e values in different solvents as follows: A, 0.6; B, 0.5; and C, 0.65.

Oligosaccharides (j) and (k)

These were eluted from charcoal by 5% ethanol and had the following R_e values: oligosaccharide (*j*), A, 0.45; B, 0.4; and C, 0.8; oligosaccharide (*k*), A, 0.40; B, 0.35; and C, 0.8.

Higher Oligosaccharides

Two further fractions were obtained from the charcoal column. One, eluted by 10–25% ethanol, contained mainly tetrasaccharides and amounted to 8.6% of the glucomannan. The other, eluted by 15–30% ethanol was 6% of the glucomannan and contained higher oligosaccharides (penta-, hexa-, hepta-). These two fractions were not examined further at this time.

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A COUNTER FOR MEASUREMENT OF TRITIUM EXCHANGE IN SOLIDS[1]

O. SEPALL,[2] A. R. G. LANG, AND S. G. MASON

ABSTRACT

An apparatus for measuring the exchange of tritium (H^3) between water vapor and solids such as cellulose has been developed which is simpler, less expensive, and more precise than an earlier model.

Both the exchange reaction and the determination of sample tritium activity are performed in a windowless, proportional counter. The background activity in sorbed water on counter surfaces is measured independently of sample activity. Satisfactory reduction of the effect of the electrostatic charge on the sample upon counting rate is achieved by the geometry of the counter.

INTRODUCTION

An exchange of hydrogen usually occurs between water and the hydroxyl groups of other substances, the extent of which can be determined by using tritiated water. The apparatus described in this paper is suitable for the measurement of exchange between water vapor and solid substances such as cellulose and is a much simpler version of a device previously described (1). The measurement consists of (1) exposing the sample to water vapor enriched with tritium, (2) removal of adsorbed water by evacuating, and (3) determination of tritium activity in the sample by a counting technique. The two main difficulties with the method are (1) the measurement of low-energy beta radioactivity from nonconductive solids and (2) elimination from the measurement, of significant background radioactivity from sorbed water on counter surfaces.

Low-energy beta radioactivity is preferably measured with a windowless counter so as to avoid attenuation of the radiation. In such a counter a nonconductive sample such as cellulose can accumulate electrostatic charge which may affect the measurement. The charge is produced by positive ions formed in the counting gas and tends to lower the counting rate by reducing the electric field intensity in the counter. An electrostatic charge was avoided in the earlier model by isolating the sample from the counting chamber by a thin conductive window (1). Bank *et al.* (2) have eliminated the charge by mixing the sample with graphite to render it conductive. The counter described here requires neither conductive window nor modification of the sample; reduction of the charge effect to an acceptable level is achieved by suitable dimensioning of the counter chamber. Windowless flow counters of special design for the detection of tritium in paper chromatograms have been described before (3, 4), but whether electrostatic charges affected counting performance could not be ascertained from the reported results.

The sorption of water on counter surfaces can result in a high contamination background activity which is included in the measurement of activity from the sample. The present counter permits the determination of the background for each measurement, and in this respect possesses a distinct advantage over the previous model (1).

DESCRIPTION

General Description of Apparatus

The apparatus shown schematically in Fig. 1 consists of the methane-filled counter and an arrangement for exposing the samples to tritiated water vapor. The counter is shown

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Contribution from the Physical Chemistry Division, Pulp and Paper Research Institute of Canada and the Department of Chemistry, McGill University, Montreal, Quebec.
[2]*Holder of a C-I-L Fellowship 1960–61.*

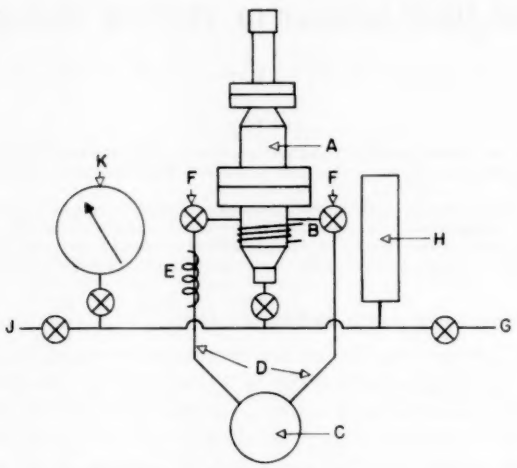

FIG. 1. Schematic drawing of apparatus.
A. Counter (methane-filled)
B. Electrical heater
C. Tritiated water reservoir
D. Copper tube
E. Electrical heater
F. High-vacuum bellows-type valve
G. Vacuum connection
H. Pirani gauge
J. Methane inlet
K. Pressure gauge (0 to 100 mm)

at A with an electrical heater on the lower section at B. The 100-ml Pyrex flask C contains 50 ml of tritiated water (1.5 μc/mg) which is stirred magnetically and is immersed in a water bath at constant temperature. Water vapor enriched with tritium is conducted over the sample through the copper tubes indicated at D. Circulation of vapor is assisted by the convection created by heating one of the tubes electrically at E. The vacuum valves F enable the counter to be isolated from the tritiated water reservoir. At G the apparatus is connected with a vacuum system consisting of a liquid-air trap, a single-stage oil diffusion pump, and a mechanical backing pump. The vacuum in the counter is measured during drying of the sample by the Pirani gauge H. The pressure of the methane gas, which is admitted through line J, is measured by gauge K.

Counter

A vertical section of the counter, which consists almost entirely of commercial fittings, is shown to scale in Fig. 2.

The body E of the counter is a copper bushing, soft soldered to the brass vacuum flanges G and C. Flange G provides access to the counter for inserting samples. Flange C supports the alloy glass insulator B, which carries the high voltage electrode with the 1-mil tungsten collector anode D. At A is shown the standard Amphenol connector for the associated preamplifier. The sample is mounted in holder F and is exposed to tritiated water vapor circulated through tubes H. The counter is evacuated through outlet J and methane counting gas is admitted through inlet K.

The sample holder is supported by two pins fitting into slots cut in the lower vacuum flange and can be rotated on the pins. Figure 3*a* shows the holder assembly in more detail. In the sectional view (A–A) the sample is shown at B, clamped in the steel ring F by the aluminum annulus C. A copper disk D is held centrally in the holder by another

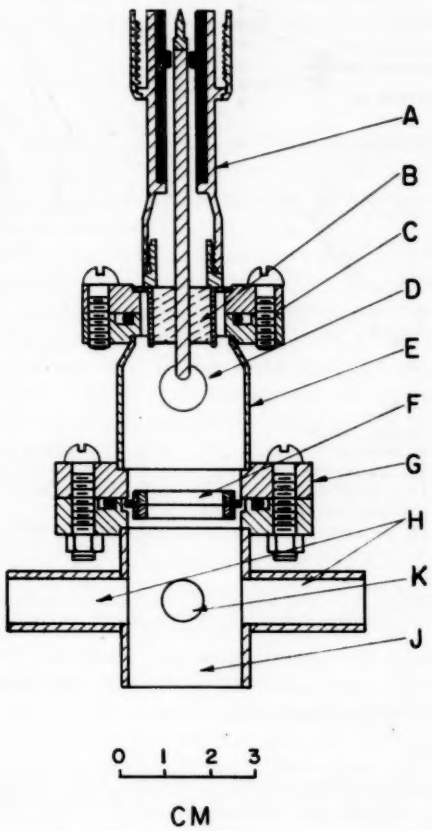

FIG. 2. Sectional view of counter.
A. Amphenol connector
B. Alloy-glass insulator (Stupakoff No. 95.0047)
C. Brass vacuum flange
D. Collector electrode
E. Copper bushing
F. Sample holder
G. Vacuum flange
H. Vapor circulation line
K. Methane inlet
J. Outlet to vacuum system

aluminum annulus G and serves to limit the electric field in the counter to the space above the sample holder.

The holder was positioned in the counter so that the closest distance from collector to copper disk was 20 mm or 74% of the diameter of the counter chamber, to satisfy a geometry requirement discussed later.

The sample is rotated and positioned from outside the counter by a magnetic field which interacts with the steel ring of the sample holder. To turn the sample over, a horseshoe magnet is directed along the axis of rotation of the holder and is rotated close to the counter through 180°. The holder is positioned by the arrangement shown in Fig. 3*b*. The vacuum flange which supports the holder is shown at L. Two iron pins K are soldered in holes drilled through the flange and extend to the inside surface. The pins are so positioned that the air gap between them and the steel ring of the sample holder

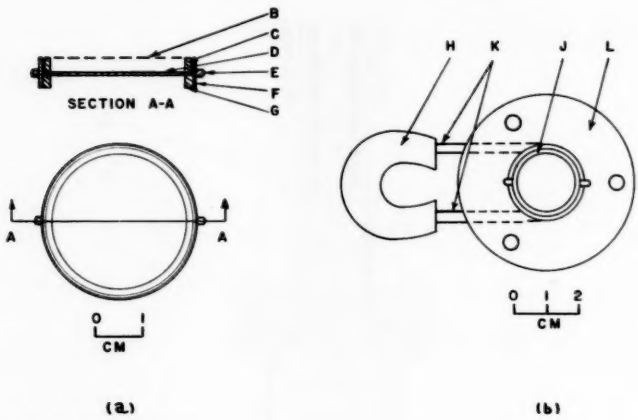

FIG. 3. (*a*) Sample holder.
B. Sample
C. Sample clamping ring
D. Copper disk
E. Supporting pin
F. Outside retaining ring
G. Clamping ring
(*b*) Sample positioning device.
H. Horseshoe magnet
K. Iron pins
J. Sample holder
L. Vacuum flange

is minimal when the holder is in the required position for counting. When the magnet H is placed on the ends of the iron pins, as shown in Fig. 3*b*, the magnetic field causes the sample holder to rotate to the counting position. There are thus two stable positions of the holder which differ by a rotation of 180° and permit the measurement of radioactivity from the sample and from the copper disk.

Experimental Procedure

The use of the apparatus is illustrated by considering the steps in a typical measurement. The sample (e.g. cellophane) was used in sheet form with a superficial density of 3 to 5 mg/cm², which corresponded to infinite thickness for beta particles from tritium.

The sample was mounted in the holder (Fig. 3*a*) and the counter assembled and evacuated. Tritiated water vapor was circulated over the sample and the relative humidity was kept constant at a desired value during the treatment. The relative humidity was determined by the sample temperature, which was kept constant by heating the counter, and by the vapor pressure in the vessel, which depended upon the temperature of the tritiated water reservoir. After the desired reaction time the counter was evacuated. It has been shown that the complete removal of water from cellulose requires heating the sample at 70° C at 1 μ Hg for many hours (5). It was possible to use these conditions for drying in the present counter, which could be heated to over 100° C, and thus to avoid the error in previous measurements from extraneous activity in sorbed water in the sample. Tritium activity was measured by counting in methane gas at 90 mm pressure. From the counting rates measured from the sample and from the copper disk, the counting rate for the sample only, was calculated by the following relationship:

$$S = M_s - (0.77 \times M_d)$$

where S is the counting rate for the sample, M_s is the counting rate measured from the sample, and M_d is the counting rate measured from the copper disk. The factor 0.77 was

determined from measurements of the background counting rate for the sample, which was found to be 77% of the counting rate measured from the copper disk and is discussed later.

GENERAL CONSIDERATIONS

Preliminary Remarks

The counter design was based on the results of preliminary studies of (1) the relationship between counter geometry and the effect of electrostatic charges on the sample upon counting rate, and of (2) the reduction of contamination background activity by the selection of a suitable counter material.

The following consideration of factors contributing to the formation of an electrostatic charge on the sample suggested its reduction by adopting a suitable geometry for the counter. The electrostatic charge is produced by positive gaseous ions which drift from the region of the collector electrode to negatively charged surfaces. Some ions strike the sample, which acquires a charge if it is nonconductive, the magnitude of the charge depending on the flux of ions impinging on the sample. To decrease this flux a greater fraction of ions must be constrained to drift to the metal wall of the counter by intensifying the electric field from collector to wall. The required modification of the electric field is achieved by decreasing the distance from collector to wall or by increasing the distance from collector to sample. The reduction of the flux of ions drifting to the sample is therefore related to a parameter $R = h/d$, where h is the least distance from collector to base at the sample position and d is the diameter of the counter. Larger values of R are associated with a more intense electric field between collector and wall. A brief study of the influence of R on the counting characteristics of a windowless counter with a cellophane source is outlined below.

Effect of Counter Geometry on Counting Performance

Four counters were constructed similar to the design described above and having values of R ranging from 0.16 to 4.6. For the two counters with lower values of R, d was 35 mm, while for the other two, d was 27 mm. The source was prepared by exposing cellophane to tritiated water vapor and drying. Counting rates were measured in methane at 90 mm pressure.

Counting rates measured in the region of the plateau with sources of equal activity are shown in Fig. 4*a* for counters with $R = 0.16$ and 0.37. The steeply rising portions

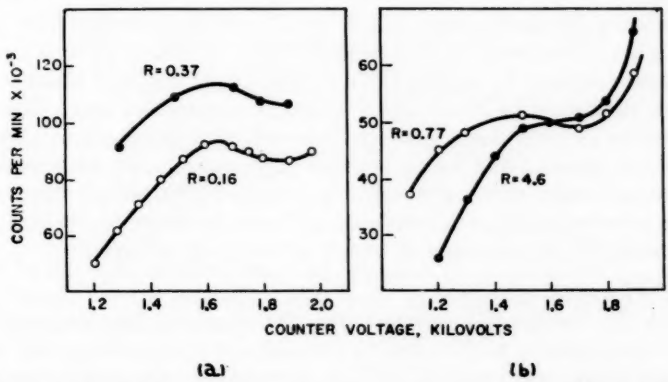

FIG. 4. Effect of R on plateau curves for cellophane sources. Source activities are different for (*a*) and (*b*).

of the curve at low and high voltages have been omitted in order to use an expanded scale for counting rates and to accentuate the differences from the usual plateau shape. A lower electrostatic charge is indicated on the sample in the counter with higher R by the higher counting rate found at all voltages. The negative slope along part of both curves suggests that a higher counter voltage results in a greater charge on the sample and the reduction of counting rate in the plateau region.

For larger values of R, the counting rates in the plateau region reach a limiting value as shown in Fig. 4*b* by the approximately equal rates measured near counter voltages of 1.55 kv for sources of equal activity and in counters with $R = 0.77$ and 4.6. For the counter with larger R, a negative slope is not found in the shortened plateau region. Although a counter with the larger R would be desirable because of the smaller effect of sample charge, the corresponding greater inside surface area results in increased background activity. The counter with $R = 0.77$ was therefore selected for use.

Counter Material

The influence of counter metal on the level of background activity was estimated by comparing background counting rates in a counter lined with a sheet of each metal. In each case the counter was exposed to tritiated water vapor and evacuated as for the measurement of tritium exchange. The measured counting rates are listed in Table I

TABLE I

Background activity from counter surfaces
$R = 0.37$

Counter material	Counts per minute
Aluminum	15,000
Nickel	57,000
Stainless steel 306	19,000
Copper	7,000

and show copper to be least contaminated of the materials tried, and for this reason was selected.

PERFORMANCE OF COUNTER

Counter Plateau

Plateau curves for the final counter with $R = 0.77$ are shown in Fig. 5 for a benzidine source with tritium incorporated by the method due to Wilzbach (6) and for a tritiated cellophane source prepared by exposing the cellophane to tritiated water and drying. The plateau for the benzidine source has a length of about 400 v and a slope of 4.4%/100 v. The plateau for cellophane appears distorted; it is displaced to higher voltage than the benzidine plateau and has a negative slope presumably because cellophane, unlike benzidine is nonconductive and acquires a residual electrostatic charge. A voltage of 1.5 kv, which corresponded to a counting rate least sensitive to changes in counter voltage, was chosen for measurement of tritium activities in cellophane.

Estimation of Background Activity

To determine the background activity from the counting rate measured from the copper disk, it was necessary to (1) estimate the counting rate resulting from the sample when the sample holder was inverted, and (2) to determine the activity on the copper disk.

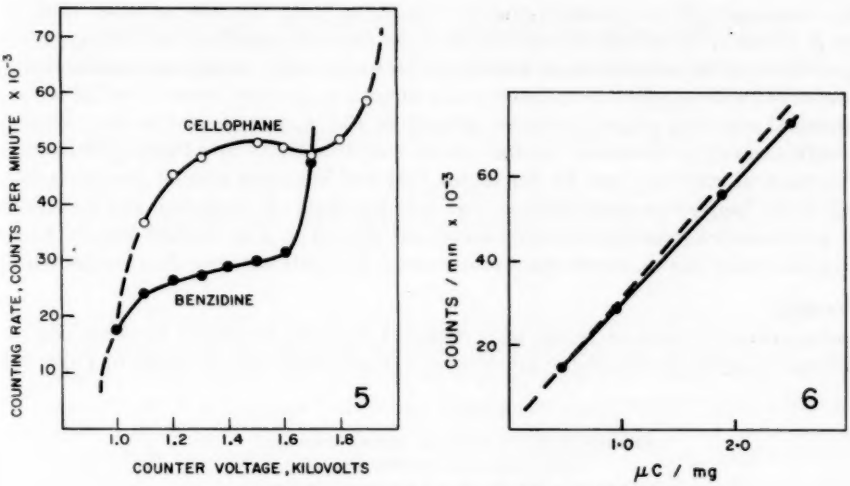

FIG. 5. Plateau curves for counter with $R = 0.77$.
FIG. 6. Sample counting rate vs. specific activity in water.

The transfer of radioactivity through the annular space between holder and counter was estimated by the following experiment. The counting rate from the copper disk was measured with and without a benzidine source of high activity (6×10^5 counts/minute) placed in the inverted sample position. The difference between the two measurements, which was ascribed to transfer of radioactivity to the counter, corresponded to less than 0.05% of source activity and could be neglected. The measured counting rates from sample and from copper disk therefore represented activities for (sample+background) and (copper disk+background), respectively.

To determine the background, a sample of zero activity was used. It was assumed that films of polyethylene, Teflon, and Saran would have no tritium activity after being exposed to tritiated water vapor and drying. Counting rates measured from the films are listed in Table II as percentage of the counting rate from the copper disk. Polyethylene

TABLE II

Ratio of background activity to activity measured with copper disk

Film used for measurement	Ratio %
Polyethylene	77
Teflon	78
Saran	80

was found to be the least contaminated and the value obtained in this case was taken to be the background. For the conditions described, the background count was 20 to 25% of the value for cellophane samples.

Calibration

Since there were indications that the counting rate measured from cellophane was affected by the residual electrostatic charge on the sample, it was desirable to determine

whether counting rate was proportional to sample activity. It was assumed that the activity of tritium in a cellophane sample, after the exchange reaction and drying, would be proportional to the isotopic concentration in the water vapor. Exchange measurements were conducted with samples of tritiated water ranging in activity from 0.5 to 2.5 μc/mg. The measured counting rates, which are plotted in Fig. 6, were found to vary linearly with specific activity in the water. An increase of specific activity by a factor 2.00 resulted in the increase of counting rate by the factor 1.96 and indicates a small deviation from proportionality between sample activity and counting rate. A correction can be readily applied to measured counting rates to eliminate the error. The dotted line in Fig. 6 shows the ideal relationship where exact proportionality exists between the two quantities.

Reproducibility

Measurements of tritium exchange were repeated with one sample of amylose film and with different samples of cellophane taken from a single sheet and are listed in Table III.

TABLE III

Reproducibility of exchange measurements on cellophane and amylose film

	Counts per minute	
Measurement	Cellophane*	Amylose†
1	43,400	55,650
2	42,100	55,710
3	43,300	55,700
4	43,500	55,400
Mean	43,100	55,620
Range	3.2%	0.54%

*Cellophane samples taken from one sheet.
†Same Amylose film used for each measurement.

The range of 0.54% in the results for amylose is indicative of good precision for the measurement. The greater range of 3.2% found in the measurements on cellophane was probably due to actual differences between samples.

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DÉRIVÉS DU TRIMÉTHYL-1,8,8 BICYCLO[3.2.1]OCTANE

VI. SYNTHÈSE DU (+)-TRIMÉTHYL-5,8,8 BICYCLO[3.2.1]OCTÈNE-2[1]

J. M. BILLY,[2] H. FAVRE ET J. M. LALANCETTE[3]

RÉSUMÉ

Les (+)-triméthyl-5,8,8 amino-2α (et 2β) bicyclo[3.2.1]octanes, le (+)-triméthyl-5,8,8 bicyclo[3.2.1]octène-2 et le (+)-triméthyl-1,8,8 bicyclo[3.2.1]octane exempts d'isomères sont décrits.

Au cours de l'étude de certaines réactions d'élimination à partir des alcools II et III (R = OH) nous avons eu besoin de triméthyl-5,8,8 bicyclo[3.2.1]octène-2 très pur et de configuration identique à celle du (+)-homoépicamphre I (R = O).[4] Pour obtenir cet hydrocarbure nous avons mis en œuvre la réaction de Tschugaeff et celle d'Hofmann.

L'un et l'autre des xanthogénates II et III (R = OCS_2CH_3), ayant un hydrogène cis par rapport à R en position 3, devaient conduire à l'hydrocarbure IV.[5, 6] Nous avons choisi de préparer et de pyrolyser le xanthogénate issu du triméthyl-5,8,8 bicyclo[3.2.1]-octanol-2α (III, R = OH), parce qu'étant équatorial l'alcool devait s'estérifier facilement. Le xanthogénate de méthyle en question se prépare aisément et sa pyrolyse conduit au (+)-triméthyl-5,8,8 bicyclo[3.2.1]octène-2 (IV) exempt d'isomères et d'une grande pureté stérique. La constitution et la pureté stérique de cet hydrocarbure furent établies par ozonolyse en acide β-homocamphorique (V) et cyclisation du sel de plomb de ce diacide en épicamphre VI, $[\alpha]_D = -57.4°$. Le pouvoir rotatoire de l'épicamphre VI, de configuration absolue identique à celle du (+)-homoépicamphre et du (+)-camphre (5, 6), est de −58°.

L'amine II (R = NH_2) nécessaire à la dégradation d'Hofmann a été préparée à partir de l'oxime de l'homoépicamphre (I, R = =N—OH). En manipulant de grandes quantités de cette oxime, nous avons pu en isoler deux variétés: p.f. 107.5–108.5°, $[\alpha]_D$ +168° et p.f. 104.5–105.5°, $[\alpha]_D = +107.8°$; il pourrait s'agir des isomères syn et anti, car les deux donnent de l'homoépicamphre par hydrolyse. Ainsi se trouve levée toute ambiguité au sujet de la différence entre les points de fusion et les pouvoirs rotatoires de l'oxime de l'homoépicamphre rapportés par Salmon-Legagneur (6) et par notre groupe; l'oxime que nous avons décrite (7) $[\alpha]_D = +125°$, est un mélange des deux isomères.

Dans un mémoire antérieur (1) notre groupe décrivait les alcools secondaires issus de la réduction du (+)-homoépicamphre I (R = O): l'alcool au platine et l'alcool au sodium reçurent respectivement les formules II (R = OH) et III (R = OH). En partant du fait—montré plusieurs fois (8, 9, 10)—que les réductions des cétones et des oximes suivent

[1]*Manuscrit reçu le 14 décembre 1960.*
Contribution du Département de Chimie de l'Université de Montréal, Montréal, Qué. Ce mémoire est tiré du rapport de maîtrise de J.M.L. et de la thèse de doctorat de J.M.B.
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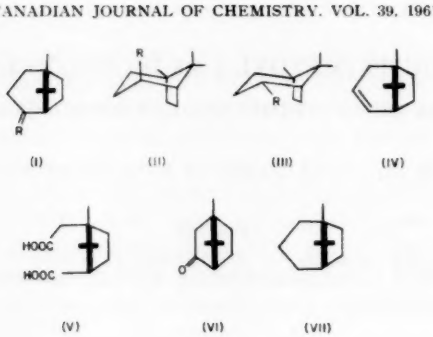
[3]*Boursier du Conseil National de Recherches du Canada, 1957–1960. Adresse: Université de Sherbrooke, Sherbrooke, Qué.*
[4]*Pour la configuration absolue du (+)-homoépicamphre, voir référence 1.*
[5]*La formation de l'isomère à double liaison sur la tête de pont est interdite (règle de Bredt).*
[6]*Pour le mécanisme d'élimination cis, voir référence 2 et pour des pyrolyses de xanthogénates sans réarrangement de squelette, voir références 2, 3, 4.*



(I) (II) (III) (IV)

(V) (VI) (VII)

le même cours stérique, nous attribuons la formule II (R = NH_2, axial) à l'amine au platine et la formule III (R = NH_2, équatorial) à l'amine au sodium; fraîchement préparées, ces amines sont des solides; celle au platine est plus dextrogyre que celle au sodium, résultat en accord avec ce que nous avons observé chez les alcools II et III (R = OH) (1); elles sont exemptes d'isomères comme le montre la chromatographie sur papier; elles sont cependant très sensibles à l'air et à l'humidité, ce qui fait que nous n'avons pu obtenir des valeurs analytiques (carbone, hydrogène et azote) satisfaisantes. Les dérivés *p*-nitrobenzoylés sont toutefois stables et facilement cristallisables: ils confirment bien la structure des amines. L'amide issu de l'amine au platine (NH_2, axial) est plus dextrogyre que celui de l'amine au sodium (NH_2, équatorial) ($[\alpha]_D$ +86.4° et +35.1° respectivement), comme c'était le cas pour les *p*-nitrobenzoates issus des alcools correspondants—$[\alpha]_D$ +78.5° (axial) et +24.5° (équatorial) (1).

Haworth, McKenna et Powell (11), puis Gent et McKenna (10) ont montré que les hydroxydes de triméthylammonium quaternaires stéroïdaux (position 3, séries 5α et 5β; position 6, série 5α) ne donnent, par pyrolyse, des hydrocarbures non saturés que s'ils sont axiaux; lorsqu'ils sont équatoriaux les auteurs ont observé une élimination de méthanol avec régénération des diméthylamino-stéroïdes correspondants. McKenna et Slinger (12), dans leur étude de la décomposition des iodures et des hydroxydes de bornyl-, et de néobornyl-, triméthylammonium quaternaires, signalent que seule la pyrolyse des hydroxydes secs conduit au bornène-2 (réaction E_2, sans réarrangement); toute autre forme de traitement augmente la proportion de camphène, de tricyclène et d'amine tertiaire correspondante. À la lumière de ces résultats il était clair qu'il fallait pyrolyser l'hydroxyde d'ammonium quaternaire issu de l'amine axiale: seul le triméthyl-5,8,8 bicyclo[3.2.1]octène-2 était à prévoir.[5]

Nous avons donc préparé l'amine diméthylée II (R = $N(CH_3)_2$) par la méthode à la formaldéhyde/acide formique; il s'est formé au cours de cette opération 49% de cétones, caractérisées par spectroscopie infrarouge; cette formation de cétones est typique pour les amines empêchées (10). La quaternisation a été effectuée par l'iodure de méthyle, à la manière habituelle; l'iodure ainsi obtenu a été transformé en hydroxyde par l'oxyde d'argent; la pyrolyse de cet hydroxyde donne 83% de (+)-triméthyl-5,8,8 bicyclo-[3.2.1]octène-2 (IV) pur, identique à celui obtenu plus haut par la méthode de Tschugaeff.

L'hydrogénation catalytique de l'oléfine IV donne le (+)-triméthyl-1,8,8 bicyclo-[3.2.1]octane (VII), que l'on obtient également par hydrogénolyse du thioacétal I (R = —S—CH_2—CH_2—S—). L'hydrocarbure saturé VII montre de petites variations dans ses propriétés physiques suivant le mode de préparation.

PARTIE EXPÉRIMENTALE[7]

1. Préparation des amines II *et* III *(*R = NH_2*)*

1.1. Oximes du (+)-homoépicamphre

On chauffe à l'ébullition à reflux: 50 g d'homoépicamphre, 50 g de chlorhydrate d'hydroxylamine, 250 ml d'éthanol et 500 ml d'une solution aqueuse d'hydroxyde de sodium à 2%. Après 10 minutes de reflux, on abandonne à 5°. Les cristaux sont essorés, lavés à l'eau et dissous dans de l'éther. La solution éthérée est lavée avec Na_2CO_3 aqueux 2% et avec de l'eau, séchée sur sulfate de sodium anhydre et évaporée; on recueille 48.5 g d'oxime brute p.f. 103.5–104°, $[\alpha]_D = +137.8°$ ($c = 4.3$; benzène).

En cristallisant cette oxime dans le mélange éthanol–eau on obtient une oxime p.f. 107.5–108.5°, $[\alpha]_D = +168.0°$ ($c = 2.2$; benzène). Calculé pour $C_{11}H_{19}ON$: C, 72.88; H, 10.56; N, 7.73%. Trouvé: C, 72.69; H, 10.44; N, 7.78%. Dans les eaux-mères on recueille, après deux cristallisations dans le mélange éthanol–eau, l'oxime p.f. 104.5–105.5°, $[\alpha]_D = +107.8°$ ($c = 2.5$; benzène). Trouvé: C, 72.70; H, 10.51; N, 7.68%.

Chacune de ces oximes (500 mg), chauffée pendant 4 heures à reflux avec 20 ml d'une solution aqueuse d'acide oxalique à 20%, donne du (+)-homoépicamphre. Les spectres infrarouges des deux oximes sont identiques, quant aux nombres d'onde des bandes; on remarque toutefois de légères différences dans les intensités des bandes situées à 873, 1007 et 1320 cm^{-1}.

*1.2. Triméthyl-5,8,8 amino-2β bicyclo[3.2.1]octane (*II, R = NH_2*)*

Une solution de 40 g d'oxime d'homoépicamphre ($[\alpha]_D^{23} = +137.5°$) dans 250 ml d'acide acétique glacial fraîchement distillé est agitée en atmosphère d'hydrogène, à pression ordinaire, en présence de 900 mg d'oxyde de platine. Au bout de 18 heures, on filtre et neutralise le filtrat par NaOH aqueux 20%. On épuise par de l'éther, extrait la solution éthérée par HCl aqueux 5%; on neutralise la solution aqueuse et extrait par de l'éther; on lave la couche éthérée jusqu'à neutralité, évapore et recueille 33.3 g d'amine brute solide.

Picrate.—Les 33.3 g d'amine brute sont dissous dans 700 ml d'éthanol; à cette solution bouillante on ajoute une solution bouillante d'acide picrique (45.6 g dans 600 ml d'éthanol). Le picrate cristallise lentement: rendement 54.5 g (69%), p.f. 253–254°, $[\alpha]_D = +30.0°$ ($c = 3.54$; DMF). Un échantillon pour l'analyse présente les constantes suivantes, après cristallisation dans le mélange DMF–méthanol 1–30: p.f. 253–254°, $[\alpha]_D = +30.7°$ ($c = 3.6$; DMF). Calculé pour $C_{17}H_{24}O_7N_4$: C, 51.51; H, 6.10; N, 14.13%. Trouvé: C, 51.41; H, 6.31; N, 14.18%. On peut obtenir jusqu'à 90% de picrate $[\alpha]_D = +30.4°$. Le rendement stérique de la réduction est donc supérieur à 90%.

Amine libre.—On traite 11.0 g du picrate par NaOH aqueux 5% (excès 100%). On extrait par de l'éther, lave à l'eau, sèche et évapore l'éther. L'amine fond à 162°, $[\alpha]_D = +61.0°$ ($c = 1.0$; EtOH 95%). Chromatographie ascendante, papier Whatman No. 1, toluène – acide acétique – eau 50–3–47, développement à la ninhydrine: tache rouge, R_f 0.88.

p-Nitrobenzamide.—Préparé par l'action du chlorure de *p*-nitrobenzoyle sur l'amine libre dans du benzène. Fines aiguilles (MeOH–eau), p.f. 125°, $[\alpha]_D^{25} = +86.4°$ ($c = 1.0$;

[7] *Les points de fusion (p.f.) ont été déterminés dans des tubes capillaires, dans un bloc chauffé électriquement et en utilisant un thermomètre étalonné avec les standards du Bureau des Standards de Washington. Les spectres infrarouges ont été mesurés à l'aide d'un spectromètre "Perkin–Elmer", modèle 21, prisme* NaCl. *Les analyses sont de M. W. Manser, Herrliberg, Suisse. Les pouvoirs rotatoires* $[\alpha]_D$ *sont à* $\pm 2°$ *près, température 23–25°. DMF = diméthylformamide.*

$CHCl_3$). Calculé pour $C_{18}H_{24}N_2O_3$: C, 68.33; H, 7.65; N, 8.85%. Trouvé: C, 68.25; H, 7.69; N, 8.92%.

1.3. Triméthyl-5,8,8 amino-2α bicyclo[3.2.1]octane (III, R = NH_2)

À une solution de 24 g d'oxime d'homoépicamphre ($[\alpha]_D^{23}$ = +137.8°) dans 1500 ml d'éthanol anhydre on ajoute 92 g de sodium, en 15 minutes, par portions de 5 g. Après l'addition on chauffe à l'ébullition à reflux pendant 30 minutes. Le tout est refroidi à 25° et dilué par un égal volume d'eau. On épuise par de l'éther et isole, comme en *1.2*, 18 g d'amine brute.

Picrate (voir section 1.2).—Dix-huit grammes d'amine brute dans 50 ml d'éthanol et 25 g d'acide picrique dans 45 ml d'éthanol donnent 30 g de picrate. Après cinq cristallisations dans le mélange DMF–méthanol (1:30) le picrate fond à 263–265° (décomposition), $[\alpha]_D$ = +22.5° (c = 2.9; DMF). Calculé pour $C_{17}H_{24}O_7N_4$: C, 51.51; H, 6.10; N, 14.13%. Trouvé: C, 51.42; H, 6.17; N, 14.23%.

Amine libre (voir section 1.2).—Le picrate (13 g) est traité à la manière décrite en *1.2*; l'amine fond à 83–84°, $[\alpha]_D$ = +25.4° (c = 1.5; EtOH 95%). R_f 0.79, tache brune (conditions expérimentales, voir section *1.2*).

p-Nitrobenzamide (voir section 1.2).—Fines aiguilles (EtOH–eau), p.f. 188–190°, $[\alpha]_D^{23}$ = +35.1° (c = 3.0; $CHCl_3$). Calculé pour $C_{18}H_{24}N_2O_3$: C, 68.33; H, 7.65; N, 8.85%. Trouvé: C, 68.23; H, 7.64; N, 8.78%.

2. Réaction de Tschugaeff

2.1. Triméthyl-5,8,8 bicyclo[3.2.1]octyl-2α xanthogénate de méthyle

Méthode de Tschugaeff (13). Dix grammes de triméthyl-5,8,8 bicyclo[3.2.1]octanol-2 (III, R = OH) (59.4 mmoles) dans 25 g de toluène anhydre sont chauffés à reflux pendant 20 heures avec 1.5 g de sodium (65 mmoles). La solution de l'alcoolate est ensuite décantée dans 100 ml d'éther anhydre et traitée par 5.0 g de sulfure de carbone (66 mmoles). Le xanthogénate de sodium qui précipite immédiatement est essoré et lavé à l'éther; il est repris dans un mélange de 100 ml d'éther et de 20 ml de méthanol et chauffé à reflux pendant 5 heures en présence de 9.6 g d'iodure de méthyle (67.5 mmoles). On lave le mélange réactionnel à l'eau, on sèche la phase éthérée sur sulfate de sodium anhydre et distille l'éther: on recueille 14.8 g de résidu; huile légèrement jaune qui, à froid, abandonne de grosses aiguilles. Le xanthogénate a été recristallisé dans de l'éthanol aqueux jusqu'à indice de rotation constant: p.f. 48.5–49.5°, $[\alpha]_D^{23}$ = +82.2° (c = 1.33; benzène), rendement 11.0 g (72%). Calculé pour $C_{13}H_{22}OS_2$: C, 60.39; H, 8.58; S, 24.81%. Trouvé: C, 60.30; H, 8.52; S, 24.97%.

2.2. Pyrolyse du xanthogénate

Sept grammes de xanthogénate (décrit en section *2.1*) sont chauffés à pression ordinaire dans un appareil à sublimation jusqu'à 220° (température du bain d'huile). Le produit de cette pyrolyse est sublimé quatre fois, afin de compléter la décomposition du xanthogénate qui contamine l'hydrocarbure isolé. On retrouve ainsi 2.0 g (49%) d'un solide blanc, $[\alpha]_D$ = +6.9° (c = 2.7; chloroforme). Ce composé est repris dans 25 ml d'éther de pétrole, et fixé sur une colonne d'alumine de 60 g préparée dans le même solvant. Une première élution par 150 ml d'éther de pétrole donne 1.75 g de triméthyl-5,8,8 bicyclo-[3.2.1]octène-2 pur (43% de la théorie); il faut l'isoler par distillation lente du solvant sous une colonne de Widmer et évaporation finale sous vide à froid; $[\alpha]_D$ = +7.0° (c = 1.8; chloroforme), p.f. 143.5–145° (tube scellé). Spectre infrarouge (nujol): Bande forte à 3030 cm^{-1} (C=C—H); bande faible à 1647 cm^{-1} (double liaison C=C); bande très forte à 710 cm^{-1}; bande forte à 680 cm^{-1}. Calculé pour $C_{11}H_{18}$: C, 87.93; H, 12.08%. Trouvé: C, 87.87; H, 12.09%.

2.3. Ozonolyse du triméthyl-5,8,8 bicyclo[3.2.1]octène-2

(Adaptation des méthodes (14, 15, 16).) Une solution de 425 mg de l'alcène décrit en section *2.2*, dans 25 ml d'éther de pétrole, est refroidie dans un bain de CO_2 et d'acétone. Un courant d'oxygène de 300 ml par minute contenant 1.2% d'ozone est amené dans la solution; l'ozonide se dépose sous forme de solide blanc amorphe. Après 20 minutes, la couleur bleue qui apparaît indique la fin de la réaction. Le solvant est évaporé à froid par un jet d'air sec et l'ozonide (masse visqueuse) est agité pendant 18 heures en présence de 8 ml d'acide acétique glacial, 8 ml d'éther, 2 ml d'eau et 500 mg de zinc en poudre.

Après l'hydrolyse, le zinc en excès et l'acétate de zinc sont essorés et lavés à l'éther; les produits organiques dans le filtrat sont isolés par addition d'eau et décantation de la phase éthérée. Après séchage sur sulfate de sodium anhydre, l'éther est éliminé par distillation lente sous une colonne de Widmer.

Le résidu aldéhydique de cette évaporation, qui contient un peu d'acide acétique, est repris dans 25 ml d'acétone; 700 mg de permanganate de potassium pulvérisé sont ajoutés à la solution bien agitée, par petites portions, à température ambiante. Après 30 minutes d'agitation, l'excès d'oxydant est détruit par 5 ml d'acide chlorhydrique aqueux 5% et quelques cristaux de bisulfite de sodium. Le bioxyde de manganèse est essoré et lavé à l'éther; l'acide β-homocamphorique brut (454 mg) est isolé du filtrat par deux lavages à la soude caustique aqueuse 5%, acidification (HCl 10%) de cette solution alcaline et réextraction par de l'éther. Après cristallisation dans l'eau on retrouve 327 mg d'acide (54% de rendement qui fond à 244–245°, $[\alpha]_D = +21.5°$ ($c = 1.8$; éthanol 95%). Une seconde recristallisation dans 3 ml de nitrobenzène (rendement de 88%) donne un échantillon d'acide qui apparaît sous la forme de fines aiguilles. P.f. 246–246.5°, $[\alpha]_D = +22.0°$ ($c = 3.1$; éthanol 95%). Calculé pour $C_{11}H_{18}O_4$: C, 61.66; H, 8.47%. Trouvé: C, 61.64; H, 8.41%.

Cet acide ne donne pas de dépression de point de fusion en mélange avec l'acide β-homocamphorique, p.f. 245.5–246.5°, $[\alpha]_D = +22.5°$ ($c = 3.5$; éthanol 95%), obtenu dans ce laboratoire d'après le mode de synthèse de Salmon-Legagneur (6). Cet auteur indique dans son mémoire: $[\alpha]_D^{18} = +27.2°$ ($c = 2.2$; éthanol), p.f. 220–222°.

2.4. Calcination du β-homocamphorate de plomb

Par la méthode de Salmon-Legagneur (6), 514 mg d'acide β-homocamphorique obtenu par ozonolyse en section *2.3* donnent un mélange d'un liquide brun et d'un solide qui est soumis à un entraînement à la vapeur d'eau: 194 mg d'un solide blanc sont entraînés. Ce solide est repris dans 15 ml d'éther de pétrole, fixé sur une colonne d'alumine de 10 g; on élue par 200 ml du même solvant: cette première fraction contient 40 mg d'un solide blanc non étudié. Une seconde élution par 100 ml d'un mélange d'éther éthylique et d'éther de pétrole (1:3) fournit 120 mg d'épicamphre (34% de rendement). Après une sublimation à pression ordinaire à 100° on retrouve 83 mg (23.4%) d'épicamphre, $[\alpha]_D = -55.2°$ ($c = 0.8$; benzène), p.f. 181–183°. Une deuxième sublimation donne un échantillon d'épicamphre; $[\alpha]_D = -57.4°$ ($c = 0.6$; benzène). Le spectre infrarouge (en solution dans CCl_4) montre une bande carbonyle à 1750 cm^{-1}. Salmon-Legagneur (6) donne p.f. 182°, $[\alpha]_D^{23} = -57.5°$ ($c = 3.6$; benzène).

3. Réaction d'Hofmann

3.1. Chlorhydrate de triméthyl-5,8,8 diméthylamino-2β bicyclo[3.2.1]octane
(II, R = $N(CH_3)_2$.HCl)

On dissout 9.64 g (57.6 mmoles) de triméthyl-5,8,8 amino-2β bicyclo[3.2.1]octane (préparé selon section *1.2*) dans 44 ml d'acide formique 98%; on chauffe à reflux pendant 2.5 heures avec 47 ml d'une solution aqueuse de formaldéhyde à 37% et 96 ml d'eau.

Le mélange réactionnel est ensuite refroidi dans un bain de glace et neutralisé par de la soude caustique aqueuse 10% (400 ml). La solution légèrement alcaline est épuisée deux fois par de l'éther; ces phases éthérées sont réunies et lavées trois fois à l'eau, puis par deux portions de 100 ml d'HCl aqueux à 5%. On obtient ainsi une fraction A (HCl aqueux) et une fraction B (éther).

Étude de la fraction A.—Par évaporation sous vide on recueille 7.036 g de chlorhydrate de triméthyl-5,8,8 diméthylamino-2β bicyclo[3.2.1]octane (II, R=$N(CH_3)_2$.HCl). Après deux recristallisations, (MeOH–éther) on obtient 1.71 g de fines aiguilles blanches, p.f. 267° (décomp.), $[\alpha]_D = +39.2°$ ($c = 2.14$; éthanol 95%). Calculé pour $C_{13}H_{26}NCl$: C, 67.36; H, 11.31; N, 6.05%. Trouvé: C, 67.22; H, 11.22; N, 6.08%.

Étude de la fraction B.—L'éther est lavé avec du carbonate de sodium aqueux à 5%, puis deux fois à l'eau et enfin séché sur sulfate de sodium anhydre. On isole, par distillation de l'éther à travers une colonne de Widmer, 4.757 g d'un solide blanc. Cette fraction neutre, qui montre dans son spectre infrarouge des bandes à 1712 cm^{-1} et 1623 cm^{-1}, n'a pas été étudiée.

3.2. Picrate du triméthyl-5,8,8 diméthylamino-2β bicyclo[3.2.1]octane

La mise en contact d'un échantillon du chlorhydrate de l'amine tertiaire obtenu en section *3.1* avec NaOH aqueux 5% en excès a donné l'amine tertiaire libre (liquide à odeur d'amine). Le picrate de cette base préparé comme en section *1.2* et recristallisé dans un mélange de méthanol et de DMF fondait à 168–169°, $[\alpha]_D = +27.4°$ ($c = 1.81$; DMF). Calculé pour $C_{19}H_{28}O_7N_4$: C, 53.76; H, 6.65; N, 13.20%. Trouvé: C, 53.68; H, 6.58; N, 13.30%.

3.3. Iodure de (triméthyl-5,8,8 bicyclo[3.2.1]octyl-2β) triméthyl ammonium quaternaire

L'amine tertiaire (686 mg; 3.52 mmoles) (isolée du chlorhydrate comme en section *3.2*) est dissoute dans 15 ml d'acétone et abandonnée en présence de 10 ml d'iodure de méthyle à température ambiante pendant 15 heures. L'iodure se dépose à l'état pur en grosses paillettes blanches allongées, p.f. 232° (décomp.), $[\alpha]_D = -16.2°$ ($c = 2.66$; méthanol). Rendement: 861 mg soit 73% de la théorie.

3.4. Triméthyl-5,8,8 bicyclo[3.2.1]octène-2 (IV)

À une solution de 1.00 g (2.95 mmoles) de l'iodure (préparé en section *3.3* ci-dessus) dans 50 ml d'eau on ajoute 1.73 g d'oxyde d'argent fraîchement précipité. Après 24 heures d'agitation à la température de la pièce, le mélange est filtré sur de la terre de diatomées et le filtrat est évaporé sous 11 mm à 60° (température du bain). L'hydroxyde du triméthyl-5,8,8 bicyclo[3.2.1]octyl-2β triméthyl ammonium obtenu de cette évaporation est chauffé à 150° dans un ballon de 200 ml surmonté d'un réfrigérant pendant 30 minutes. L'alcène solide, qui s'est déposé au bas du réfrigérant est repris par de l'éther de pétrole. La phase organique est lavée avec HCl aqueux 2%, avec du carbonate de sodium aqueux à 2% et à l'eau, puis séchée sur sulfate de sodium. La distillation lente du solvant à travers une colonne de Widmer abandonne 367 mg de triméthyl-5,8,8 bicyclo[3.2.1]-octène-2 (83% de rendement).

Une sublimation à 100° à pression ordinaire donne 292 mg d'alcène pur, p.f. 144°, $[\alpha]_D = +7.04°$ ($c = 6.45$; chloroforme). Le spectre infrarouge de cet échantillon est identique à celui du même alcène obtenu en section *2.2*. Calculé pour $C_{11}H_{18}$: C, 87.93; H, 12.08%. Trouvé: C, 87.89; H, 12.14%.

4. (+)-Triméthyl-1,8,8 bicyclo[3.2.1]octane (VII)

4.1. Hydrogénation du triméthyl-5,8,8 bicyclo[3.2.1]octène-2

À 438 mg de triméthyl-5,8,8 bicyclo[3.2.1]octène-2 en solution dans 15 ml d'éthanol

95% on ajoute 500 mg de nickel de Raney. Après 2 heures d'hydrogénation à pression ordinaire, 77 ml d'hydrogène sont fixés (calculé 74.6 ml; 743 mm, 23°). Le catalyseur est essoré et le produit de réduction précipité du filtrat par addition d'eau. Le triméthyl-1,8,8 bicyclo[3.2.1]octane (VII) est repris par de l'éther de pétrole. L'évaporation du solvant sous une colonne de Widmer (rendement 286 mg) et une sublimation à pression ordinaire, à 100°, conduisent à l'hydrocarbure, p.f. 168.5–169.5° (tube scellé), $[\alpha]_D = +20.3°$ ($c = 1.5$; chloroforme). Calculé pour $C_{11}H_{20}$: C, 86.67; H, 13.32%. Trouvé: C, 86.65; H, 13.15%.

4.2. Triméthyl-5,8,8 éthylène-thio-acétal-2 bicyclo[3.2.1]octane
(I, R = —S—CH_2—CH_2—S—)

On refroidit à 0° un mélange de 6.5 g (42 mmoles) de (+)-homoépicamphre et de 4.4 g (47 mmoles) d'éthanedithiol dans un ballon de 50 ml. On y fait passer un courant de HCl sec pendant 2 heures. L'excès d'acide chlorhydrique est éliminé en plaçant le ballon dans un dessicateur contenant des pastilles d'hydroxyde de sodium, et dans lequel on maintient une pression de 11 mm. On agite ensuite le mélange avec une solution aqueuse de soude caustique à 2%, on sèche sur sulfate de sodium anhydre et distille. On recueille 8.39 g (rendement de 83%) de thio-acétal p. éb. 125° sous 0.7 mm, $n_D = 1.5642$. Calculé pour $C_{13}H_{22}S_2$: S, 26.05%. Trouvé: 26.21%.

4.3. Hydrogénolyse du thio-acétal

On chauffe à l'ébullition à reflux une solution de 0.543 g du thio-acétal décrit en section *4.2* dans 35 ml de dioxanne en présence de 15 g de nickel Raney saturé d'hydrogène. Ce catalyseur fut préparé selon les indications de Mozingo *et al.* (17). Temps de chauffage: 12 heures. La réduction terminée, on essore le catalyseur et précipite le triméthyl-1,8,8 bicyclo[3.2.1]octane (VII) du filtrat par addition d'eau. Après essorage et sublimation, cet hydrocarbure présente les constantes suivantes: p.f. 163–164°, $[\alpha]_D = +15.5°$ ($c = 2.75$; EtOH 95%). Calculé pour $C_{11}H_{20}$: C, 86.67; H, 13.32%. Trouvé: C, 86.76; H, 13.24%.

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SYNTHESIS OF SYMMETRICAL AND UNSYMMETRICAL DIALKYLPHOSPHINOUS CHLORIDES[1]

J. L. FERRON

ABSTRACT

A series of compounds with the generalized formula RR'PCl have been obtained by the metal (antimony or zinc) reduction of $[RR'PCl_3]^+[AlCl_4]^-$. The yields of symmetrical and unsymmetrical dialkylphosphinous chlorides obtained by this method are superior to those obtained in previous syntheses.

INTRODUCTION

The original synthesis of symmetrical dialkylphosphinous chlorides (R = C_2H_5, *i*-C_3H_7, *i*-C_4H_9) has been the pyrolysis of R_3PCl_2 (1),

$$R_3PCl_2 \xrightarrow{\text{heat}} R_2PCl + RCl.$$

The diethyl analogue has also been obtained in 38% yield by the action of lead tetraethyl upon ethylphosphonous dichloride (2),

$$C_2H_5PCl_2 + (C_2H_5)_4Pb \rightarrow (C_2H_5)_2PCl + (C_2H_5)_3PbCl.$$

The complex resulting from alkyl chlorides, phosphorus trichloride, and aluminum chloride was first prepared by Clay (3) and formulated as

$$RCl + PCl_3 + AlCl_3 \rightarrow [RPCl_3]^+[AlCl_4]^-.$$

The above complexes have been used in these laboratories for the preparation of alkylphosphonous dichlorides (4). These dichlorides have been obtained in good yield when the aluminum chloride complex is dissolved in a high-boiling electron-donating solvent such as diethyl phthalate (DEP) and reduced with antimony powder. The diethyl phthalate apparently forms a more stable complex with the aluminum chloride and the liberated $RPCl_4$ is then reduced by the antimony powder as follows:

$$[RPCl_3]^+[AlCl_4]^- + DEP \rightarrow [DEP][AlCl_3] + RPCl_4$$

$$3RPCl_4 + 2Sb \rightarrow 3RPCl_2 + 2SbCl_3.$$

Since then Ivin and Karavanov (5) have shown that alkylphosphonous dichlorides react with aluminum chloride in an analogous fashion,

$$RPCl_2 + AlCl_3 + R'Cl \rightarrow [RR'PCl_3][AlCl_4],$$

and it occurred to us that the reduction of this complex might provide a simple and direct route to dialkylphosphinous chlorides. The reduction of a DEP solution of these aluminum chloride complexes by zinc dust at room temperature or by antimony powder at 75–80° C has provided dialkylphosphinous chlorides in yields of 60–73%.

EXPERIMENTAL

Apparatus

The apparatus used is shown in the figure and allows dialkylphosphinous chlorides to be prepared and distilled without coming in contact with air. The 10/30 Standard

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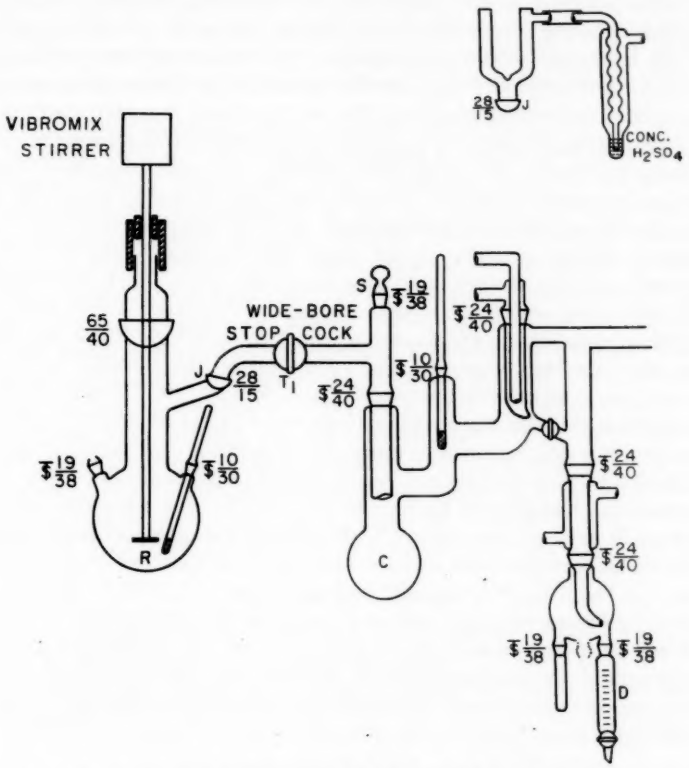

FIG. 1. Apparatus for the preparation of dialkylphosphinous chlorides.

Taper joint carries a thermometer and the 19/38 joint can be used for fitting an inlet tube, a dropping funnel, a bleed for distillations under reduced pressure, or for adding the powdered metal for the reduction. The 28/15 ball joint, J, accommodates the dry ice condenser (upper right of figure) during methyl chloride addition, or a water-cooled condenser during the addition of less volatile alkyl chlorides, as well as the distillation unit shown in the figure. Complexes described under (*a*) and (*b*) were formed in a pressure bottle and transferred into the flask R under a stream of dry N_2; those described under (*c*) and (*d*) were formed at atmospheric pressure directly in the reaction vessel R. All reactions were carried out under a dry N_2 atmosphere.

Reagents

All the reagents were of Reagent Grade and were used as supplied from the manufacturers without further purification. Antimony in lump form was ground in a mortar, pulverized in a ball mill, and sieved through a 250 mesh sieve immediately prior to use.

(*a*) *Preparation of Chloromethyl-methylphosphinous Chloride* $(ClCH_2)(CH_3)PCl$

Aluminum chloride (100 g, 0.75 mole) was weighed directly into a pressure bottle and cooled in a dry ice–acetone mixture. To the cold contents were then added chloromethylphosphonous dichloride (113.8 g, 0.75 mole) and liquid methyl chloride (40 ml,

0.80 mole). The bottle was stoppered and left standing at room temperature for 16 hours by which time the mixture had turned solid except for a small liquid layer in the bottom of the container. The contents were then heated at 100–102° C for a further 72 hours. After cooling in dry ice–acetone mixture the bottle was opened, the solid broken into pieces and transferred into the reaction flask R under a stream of dry N_2. Diethyl phthalate (DEP) (500 ml) was then added and violent stirring maintained until the solid had completely dissolved. The solution was then degassed under reduced pressure (water vacuum) while the temperature was gradually raised to 60° C. After the solution was cooled to room temperature, dry N_2 was admitted into the system, a dry ice–acetone cooling mixture placed under the receiver C, the wide-bore isolation stopcock closed, and the system evacuated to 0.1–0.5 mm. Finely powdered antimony (60.9 g, 0.5 mole) was added all at once through a Standard Taper joint, a bleed inserted, and the suspension vigorously stirred. The reaction flask R was rapidly evacuated by opening the wide-bore stopcock. The reduction of the complex by antimony was exothermic and the temperature rose slowly from 33° C to 49° C while the chloromethyl-methylphosphinous chloride distilled over into the distillation flask C. When the evolution of heat had stopped, the temperature of the solution was brought up to 80–85° C with the help of a heating mantle and maintained in that range for ½ hour. After all the dialkylphosphinous chloride had been collected, dry N_2 was admitted into the system, a bleed inserted in place of the stopper S, the isolation stopcock closed, and the product redistilled under reduced pressure, and the main fraction collected in one of the receivers. The yield of $(ClCH_2)(CH_3)PCl$ (b.p. 59° C/9 mm) was 72 g (73%). Most of the dialkylphosphinous chlorides are very reactive and cannot be handled readily in an open atmosphere. Analyses are thus cumbersome to perform and most of the compounds prepared have been identified by the formation of derivatives. $(ClCH_2)(CH_3)PCl$ was reacted with sulphur and the chloromethyl-methylthionophosphonic chloride analyzed. Calculated for $(ClCH_2)(CH_3)P(S)Cl$: C, 14.73%; H, 3.10%. Found: C, 14.84%; H, 3.20%.

(b) Preparation of Dimethylphosphinous Chloride $(CH_3)_2PCl$

This compound was prepared on a 0.75 mole scale by mixing in the cold methylphosphonous dichloride, aluminum chloride, and methyl chloride in a pressure bottle and shaking the mixture at room temperature. The complex formed readily and after transfer of the solid into the flask R and solution in DEP, the reduction by antimony (60.9 g, 0.50 mole) at 85–90° C gave 43.7 g (60%) of dimethylphosphinous chloride (b.p. 72–74° C/697 mm). The oxygen addition compound was analyzed for identification purposes. Calculated for $(CH_3)_2P(O)Cl$: C, 21.35%; H, 5.38%. Found: C, 21.33%; H, 5.33%.

(c) Preparation of Isopropyl-methylphosphinous Chloride $(i\text{-}C_3H_7)(CH_3)PCl$

For this preparation the reaction flask R was fitted with a dropping funnel in the 19/38 Standard Taper joint and the dry-ice condenser on the 28/15 ball joint J. Aluminum chloride (66.7 g, 0.5 mole) was placed in the reaction flask and isopropylphosphonous dichloride (73.0 g, 0.5 mole) was added dropwise while stirring violently. The addition was exothermic and the aluminum chloride dissolved completely. The solution was cooled to room temperature and the dropping funnel replaced by an inlet tube extending below the surface of the liquid. Slow addition of gaseous methyl chloride was started while the temperature of the reaction mixture was kept below 45° C by intermittent immersion of the flask in a cold-water bath. The addition of methyl chloride was stopped after the reaction was completed as evidenced by a fast reflux rate of methyl chloride on the dry ice condenser. The addition was complete in approximately 1½ hours. After

cooling to room temperature, the complex was dissolved in DEP (300 ml), degassed under reduced pressure, and the reduction carried out in the usual way using a theoretical amount of freshly powdered antimony (40.5 g, 0.33 mole). The yield of isopropylmethylphosphinous chloride (b.p. 82–85° C/208 mm) was 44.0 g (65.5%).

(d) Preparation of Diisopropylphosphinous Chloride $(i\text{-}C_3H_7)_2PCl$

Aluminum chloride (68.5 g, 0.51 mole) was placed in the flask R and isopropylphosphonous dichloride (74.8 g, 0.52 mole) added dropwise, the temperature being kept below 30° C by occasional immersion in a dry ice–acetone cooling bath. After the aluminum chloride had dissolved, isopropyl chloride (40.5 g, 0.51 mole) was added dropwise maintaining the temperature below 30° C. After about two-thirds of the isopropyl chloride had been added, the reaction mixture became very viscous and stirring became inefficient. The addition of isopropyl chloride was stopped, methylene chloride (50 ml) was added after which the addition of isopropyl chloride was resumed. This addition could be carried out rapidly as no appreciable heat was evolved. Once the addition was completed, the solution was heated to reflux for 1 hour, cooled to room temperature, DEP (300 ml) added with stirring, and the solution degassed in the usual way. After degassing, zinc dust (32 g, 0.51 mole) was added and the suspension heated to 45° C. An exothermic reaction set in, the heating source was removed and the reaction mixture reached a temperature of 78° C. The liquid collected in flask C was then redistilled, giving a yield of 51.2 g (67.2%) of product (b.p. 69° C/697 mm).

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HYDROXY FATTY ACID GLYCOSIDES OF SOPHOROSE FROM TORULOPSIS MAGNOLIAE[1]

P. A. J. Gorin, J. F. T. Spencer, and A. P. Tulloch

ABSTRACT

The oil formed during fermentation by a strain of *Torulopsis magnoliae* consisted mainly of partly acetylated 2-*O*-β-D-glucopyranosyl-D-glucopyranose units attached β-glycosidically to 17-L-hydroxyoctadecanoic and 17-L-hydroxy-9-octadecenoic acids.

A strain of osmophilic yeast, *Torulopsis magnoliae*, isolated from sow thistle petals, was found to produce (1) an extracellular, heavier than water oil. The main components of the oil are now shown to be glycolipids (I and II) consisting of 2-*O*-β-D-glucopyranosyl-D-glucopyranose units linked β-glycosidically to 17-L-hydroxyoctadecanoic and 17-L-hydroxy-9-octadecenoic acids, the sugar moieties being partly acetylated.

The oil was labile both to acid and alkali. Hot methanolic sodium methoxide removed the acetyl groups, which constituted about 1.5 substituent groups per mole (the positions of these substituents were not determined). The deacetylated product, after fractionation, yielded a solid (I and II),which contained almost equal quantities of lactonic and acidic glycolipids, and it was on this mixture that the characterization studies of the sugar portion were carried out.

Acid methanolysis of the deacetylated oil yielded 2 moles of methyl-α-D-glucopyranoside and 1 mole of a mixture of fatty acid methyl esters. Gas – liquid phase chromatography of the esters on a silicone column showed one principal peak at the C_{20} saturated position with a shoulder suggesting partial resolution of saturated and unsaturated esters (2). However, on a butanediol succinate column (3) no peaks appeared after 2 hours (normal emergence time for a C_{20} ester was 30 minutes). The properties suggested that the major compounds present were C_{18} esters containing a polar substituent, such as a hydroxyl group (4) and the presence of the latter group was confirmed by infrared spectroscopy. From the quantity of permanganate–periodate reagent (5) consumed, the mixture was shown to contain 65% of monoolefinic ester. Fractional crystallization of the methyl esters also yielded 65% unsaturated and 35% saturated ester. However, later fermentations contained only about 10% of the saturated material. Catalytic hydrogenation showed that the unsaturated C_{18} ester (IV) contained one double bond and the product obtained was identical with the saturated C_{18} component (III). The position of the hydroxyl group in these compounds was shown to be at C_{17}, by the formation of 17-oxostearic acid (V) when the saturated acid was oxidized with chromium trioxide. An authentic specimen of V was synthesized by the method of Bergström *et al.* (6) from 15-bromopentadecanoic acid. The latter was prepared from 15-hydroxypentadecanoic acid which was in turn obtained from the 15,16-dihydroxypalmitic acid described by Lemieux (7).

The unsaturated component (IV) was shown to be 17-hydroxy-9-octadecenoic acid methyl ester since the acid on oxidation with permanganate–periodate (5) yielded azelaic

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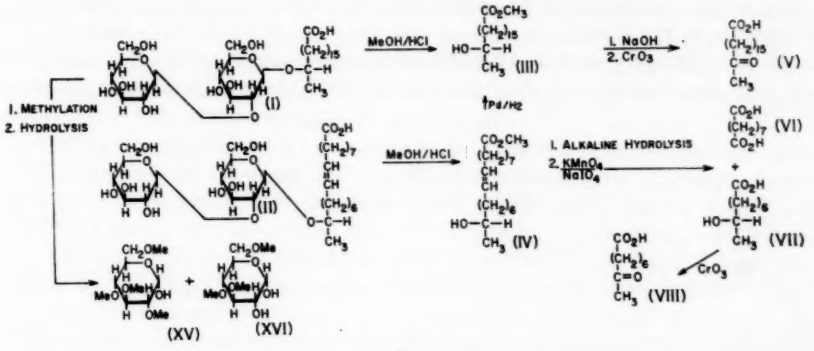
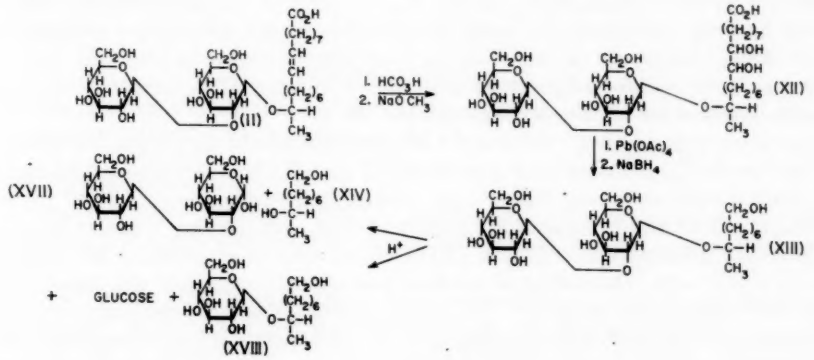


1*a*



1*b*

FIGS. 1*a* and 1*b*. Degradation of sophorosides of 17-hydroxyoctadecanoic and 17-hydroxy-9-octadecenoic acids.

(VI) and 8-hydroxy-pelargonic acids (VII). These oxidation products could not be separated by crystallization and an attempt to separate the mixture of monomethyl azelate and hydroxy acid obtained by oxidation of the methyl ester in aqueous tertiary butanol (8) was also unsuccessful. Dimethyl azelate and methyl hydroxypelargonate were not well resolved by gas chromatography on a silicone column but conversion to the corresponding *n*-butyl esters gave a mixture which was easily separated preparatively. Oxidation of sirupy 8-hydroxypelargonic acid gave crystalline 8-oxopelargonic acid (VIII) with the same melting point as that reported by Barger *et al.* (9) for the synthetic acid. The double bond (IV) was considered to have the cis configuration as the infrared spectrum had no band in the 10.36 μ region (10).

The asymmetric center at carbon-17 has been provisionally assigned the L-configuration since the specific rotation of 17-hydroxyoctadecanoic acid was +4.4°. Assuming that the carboxyl group at the end of a long methylene chain has no more effect on the specific rotation than a methyl group the saturated C_{18} hydroxy acid can be regarded as a D-carbinol (IX) of which all known members of the type depicted are dextrorotatory (XI) (11). When the structure is written as (X) it has the L-configuration according to the usual rules of nomenclature (12). Further the acid might be expected to have the

same configuration as synthetic 12-L-hydroxyoctadecanoic acid ($[\alpha]_D$ +0.8°) (13) as the sign of rotation is the same.

15-D-16-Dihydroxy- and 2-D-15-D-16-trihydroxyhexadecanoic acids isolated from ustilagic acid also possess a hydroxyl group on the penultimate carbon atom and all

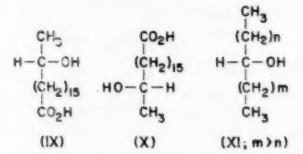


FIG. 2. Hydroxyl configuration in 17-L-hydroxydecanoic acid when regarded as an alcohol.

the optical centers were assigned the D-configuration (7), otherwise acids hydroxylated in this position do not seem to have been found in nature. For saturated acids the common positions for hydroxyl substitution are C_2, C_9, C_{10}, and the terminal carbon atom (14). Only two hydroxy monoenoic C_{18} acids have been reported, 12-hydroxy-9-octadecenoic acid, the major component of castor oil (14), and also occurring in ergot oil (15), which has been assigned the D-configuration (13), and 9-hydroxy-12-octadecenoic acid which is found in the seed fat of *Strophanthus* species (16).

To characterize the linkage types and configurations of the glycosidic linkages in the two disaccharide-C_{18} hydroxy acid glycolipids (I and II) it was necessary to separate them. Since fractionation was difficult the unsaturated portion was modified by oxidation. Treatment of the mixture with performic acid, followed by alkaline hydrolysis, gave *threo*-9,10-dihydroxy derivatives (XII) which were then oxidized by lead tetraacetate in acetic acid. The uptake of oxidant was almost immediate and indicated that 30% of the mixture was olefinic.* The resulting aldehydes were reduced with sodium borohydride, mainly to ω-hydroxypelargonic acid and a crystalline nonanediol sophoroside (XIII). These components were readily separable from the water-insoluble solid containing the 17-hydroxyoctadecanoic acid sophoroside (I). Complete acid hydrolysis of the nonanediol sophoroside yielded glucose and syrupy 1,8-nonanediol (XIV) from which a crystalline bis-*p*-nitrobenzoate was derived. The specific rotation of the diol was positive (+6.5°) indicating an L-hydroxy configuration (11) thus agreeing with the L-configuration already assigned to 17-hydroxy-9-octadecenoic acid. Complete methylation of the nonanediol sophoroside followed by acid hydrolysis gave equimolar amounts of 2,3,4,6-tetra-*O*-methyl-D-glucose (XV) and 3,4,6-tri-*O*-methyl-D-glucose (XVI), which would be expected from two glucose units linked 1,2-glycosidically. Partial acid hydrolysis of nonanediol sophoroside furnished a mixture, from which sophorose (XVII; 2-*O*-β-D-glucopyranosyl-D-glucose) and 1,8-L-nonanediol-β-D-glucopyranoside (XVIII) were isolated by cellulose chromatography (17). The negative rotation of the glycoside indicated a β-configuration for the glucose – fatty acid linkage, as well as that of the glucose-to-glucose linkage. This agrees with the observation that the nonanediol sophoroside was totally hydrolyzed by emulsin, a β-glucosidase.

The amorphous material containing mainly 17-hydroxyoctadecanoic acid sophoroside (I) was similarly methylated and hydrolyzed to yield equimolar amounts of 2,3,4,6-tetra-*O*-methyl-D-glucose (XV), 3,4,6-tri-*O*-methyl-D-glucose (XVI), and 17-L-hydroxyoctadecanoic acid. Although this evidence showed an analogous structure to the 17-L-hydroxy-9-octadecenoic acid sophoroside, the sodium salt was not hydrolyzed by emulsin.

**Since the proportion of unsaturated acid in the solid glycolipid is much less than in the parent oil (65%) it was evident that fractionation had taken place during isolation.*

However, Pigman and Richtmyer (18) note that the effect of emulsin on *n*-alkyl glucosides begins to decrease when the alcoholic aglycones have more than seven carbon atoms. The molecular rotations of the 17-hydroxyoctadecanoic acid (−14,200°, sodium salt) and 1,8-nonanediol sophorosides (−14,500°) agree closely and point to the likelihood that all the glucosidic linkages present are of the β-type.

The 2-*O*-β-D-glucopyranosyl-D-glucopyranose disaccharide unit is a unique structure in microbial metabolites. However, polysaccharides consisting of 1,2-β-D-glucopyranose units are known to be formed by various species of agrobacteria (19, 20, 21). The glycolipid molecule is similar in over-all structure to the ustilagic acids of Haskins (22) characterized by Lemieux *et al.* (7, and references cited therein) as partly acylated β-cellobiosides of 15-D-16-dihydroxyhexadecanoic and 2-D-15-D-16-trihydroxyhexadecanoic acids. Also similar is the acidic glycolipid formed by *Pseudomonas aeruginosa* which was isolated and identified by Jarvis and Johnson (23). This compound consists of a 3-*O*-L-rhamnopyranosyl-L-rhamnopyranose moiety attached glycosidically to a dimeric form of 3-D-hydroxydecanoic acid.

EXPERIMENTAL

Evaporations were carried out under reduced pressure using a bath temperature of 50° C. Optical rotations were measured at 26° C.

Method of Oil Production

The osmophilic yeast, obtained from the petal portion of a sow thistle, was shown to be a strain of *Torulopsis magnoliae* by carbon assimilation tests (1), and was designated strain N_1c.

The medium used consisted of glucose (20%), yeast extract (1.25%), and urea (0.2%) and was agitated at 385 r.p.m. for 8–10 days with an air flow rate of 500 ml/min, and incubated at 30° C in 5-l. New Brunswick fermentors (3-l. working volume). The maximum yield of the oil was about 5% of the volume of the medium and was recovered by allowing it to stand in a separatory funnel until it all settled out.

The aqueous portion of the solution was shown to contain D-mannitol, which is a common product of *Torulopsis magnoliae*, and this was obtained by crystallization of the evaporated residue from methanol. It had m.p. and mixed m.p. 166–167° C.

Deacetylation of the Oil

The oil (240 g), which contained a considerable proportion of water, was dissolved in 10 volumes of ethyl acetate. The solution was dried with $MgSO_4$, filtered, and evaporated to a yellow-brown viscous acidic syrup (148 g); C, 57.2%; H, 8.2%. It was shown to contain C—H, O—H, and carbonyl groups by infrared analysis. When saponified with alkali in aqueous ethanol it had a sap. equiv. of 226. The hydrolyzate was acidified and distilled to give acetic acid (10.2% of oil by weight).

The purified oil (115 g) was dissolved in refluxing methanol (2 l.) and sodium metal was added until the solution became alkaline. Refluxing was continued for 30 minutes, then the solution was evaporated to a syrup and the methanol distillate, which contained the methyl ester of the acetic acid, was collected in a dry-ice trap. Potassium hydroxide (1 g) dissolved in water (5 ml) was added to part of the methanol distillate and refluxed for 2 hours; after the methanol was taken off the residue was diluted with water and made just acid to phenol red by addition of hydrochloric acid. This solution was allowed to react with S-benzyl thiouronium chloride and gave S-benzyl thiouronium acetate, m.p. 131–134° C, which was not depressed by an authentic sample.

The deacetylated syrup was dissolved in water and acidified with formic acid. A gelatinous precipitate formed and after storage of the liquid at 3° C for a week it was filtered off, washed with cold water, and dried *in vacuo*. The light brown powder (44 g) had m.p. 137–139° C and analyzed as a hexose disaccharide attached glycosidically to a C_{18} hydroxy fatty acid. Roughly half of the material appeared to be in a lactonic form. Calculated for the saturated acid glycoside $C_{30}H_{56}O_{13}$: C, 57.6%; H, 9.0%; sap. equiv., 624. Found: C, 58.2%; H, 8.9%; sap. equiv., 652; neutral equiv., 1213.

Acid Hydrolysis of the Deacetylated Oil

The deacetylated syrup was refluxed with a large excess of 4% methanolic hydrogen chloride for 18 hours, then diluted with water and the fatty acid esters extracted with chloroform. The aqueous layer was neutralized (silver carbonate), filtered, and concentrated to a syrup which on crystallization from ethanol gave methyl-α-D-glucopyranoside, m.p. and mixed m.p. 166–167° C and $[\alpha]_D$ +160° (*c*, 1.0, H_2O).

Gas–liquid chromatography of the crude methyl ester on 1:6 silicone on Celite in a 6 ft×¼ in. copper column at 235° C suggested the presence of 75% saturated and unsaturated hydroxy C_{18} esters. On oxidation with permanganate–periodate the crude acid, obtained by saponification, consumed 2.6 moles of oxidant corresponding to 65% of unsaturated esters.

17-Hydroxystearic Acid

A solution of the crude fatty acid methyl esters (15.62 g) in petroleum (b.p. 60–80° C) (225 ml) was stored at +2° C for 2 days and a crystalline product (3.97 g) was obtained. This solid was distilled, b.p./0.08 mm 180° C (bath), and repeatedly crystallized from petroleum (b.p. 60–80° C) but did not yield a completely pure ester. Saponification, isolation of the acid, and crystallization from acetone gave 17-hydroxystearic acid, m.p. 78–80° C. Calculated for $C_{18}H_{36}O_3$: C, 71.9%; H, 12.1%; neutral equiv., 300.5. Found: C, 71.8%; H, 11.95%; neutral equiv., 298; $[\alpha]_D$ +4.4° (*c*, 7.9, CH_3COOH). Methyl-17-hydroxystearate was prepared from the acid with diazomethane and crystallized from petroleum (b.p. 60–80° C) as platelets, m.p. 51–53° C. Calculated for $C_{19}H_{38}O_3$: C, 72.6%; H, 12.2%. Found: C, 72.2%; H, 12.1%; $[\alpha]_D$ +4.6° (*c*, 7.3, MeOH).

17-Hydroxy-cis-9-octadecenoic Acid

The solvent was removed from part of the mother liquors of the first crystallization of the crude saturated ester and the residue distilled, b.p./0.1 mm 150° C. After saponification a further small quantity of saturated acid was removed by crystallization from petroleum (b.p. 60–80° C) containing 8% acetone at 0° C and crystallization at −20° C gave almost pure unsaturated acid, m.p. 5° C. Distillation gave the pure acid as a colorless viscous oil, b.p./0.04 mm 160° C (bath). Calculated for $C_{18}H_{34}O_3$: C, 72.4%; H, 11.5%. Found: C, 72.35%; H, 11.3%; $[\alpha]_D$ +4.3° (*c*, 6.1, MeOH). There was no absorption band in the 10.36 μ region of the infrared spectrum. The methyl ester was prepared and had b.p./0.04 mm 145° C (bath). Calculated for $C_{19}H_{36}O_3$: C, 73.0%; H, 11.6%. Found: C, 72.8%; H, 11.5%; $[\alpha]_D$ +3.5° (*c*, 6.5, MeOH).

Hydrogenation of Methyl-17-hydroxy cis-9-Octadecenoate

The crude unsaturated ester (4.95 g) was recovered from the solvent remaining after crystallization of the saturated ester and was hydrogenated in ethanol (60 ml) in the presence of 5% palladium on charcoal (0.5 g). The volume of hydrogen absorbed at N.T.P. was 293 ml; calculated for the reduction of one double bond 353 ml. 17-Hydroxystearic acid was obtained on saponification and crystallized from acetone, m.p. 78.5–80.5° C,

mixed m.p. with natural saturated acid was 78–80° C. Calculated for $C_{18}H_{36}O_3$: C, 71.9%; H, 12.1%; neutral equiv., 300.5. Found: C, 71.8%; H, 11.95%; neutral equiv., 300; $[\alpha]_D$ +4.1° (*c*, 10.0, CH_3COOH). The derived methyl ester had a melting point of 50.5–51.5° C and the mixed melting point with natural saturated ester was 50.5–52.5° C. Calculated for $C_{19}H_{38}O_3$: C, 72.6%; H, 12.2%. Found: C, 72.4%; H, 12.0%; $[\alpha]_D$ +4.2° (*c*, 9.5, MeOH).

17-Oxostearic Acid

A solution of chromic oxide (2.4 g) in water (5 ml) was diluted with glacial acetic acid (25 ml) and added portionwise to a solution of 17-hydroxystearic acid (8.0 g), prepared by hydrogenation of the unsaturated ester, in acetic acid (80 ml) maintained at room temperature. After 30 minutes the mixture was poured into water (500 ml), the excess oxidant was reduced with sulphur dioxide and the product (6.8 g) was collected, washed, and dried. Crystallization from ethanol gave the pure acid, m.p. 86–87.5° C. Calculated for $C_{18}H_{34}O_3$: C, 72.4%; H, 11.5%. Found: C, 72.2%; H, 11.35%. The acid gave a positive iodoform test. A mixed melting point with 15-oxostearic acid (24) (m.p. 83° C) was depressed to 76–85° C. The melting point was not depressed by synthetic 17-oxostearic acid (m.p. 86.5–87.5° C) and the X-ray powder photographs were indistinguishable. The methyl ester was prepared and crystallized from petroleum as leaflets, m.p. 55–57.3° C, undepressed by admixture with the synthetic ester of m.p. 54.5–56.5° C. Calculated for $C_{19}H_{36}O_3$: C, 73.0%; H, 11.6%. Found: C, 72.9%; H, 11.5%. The infrared spectra and the X-ray powder photographs of the synthetic and natural esters were indistinguishable. 17-Oxostearic acid was similarly prepared from the naturally saturated acid and did not depress the melting point of the above oxo acid.

Oxidation of 17-Hydroxy-cis-9-octadecenoic Acid

The acid (1.73 g) was dissolved in 2% potassium carbonate solution (200 ml) and added all at once to the stock oxidant solution (400 ml, containing 20.86 g sodium metaperiodate and 0.4 g potassium permanganate per liter (5)) diluted with water (1400 ml) and shaken for 4 hours. The excess oxidant was destroyed with sodium metabisulphite, the mixture acidified with sulphuric acid, and the products extracted with ether and the ether removed without drying leaving the mixture of acids (1.88 g). The mixture was taken up in ethyl acetate (10 ml) when part of the azelaic acid (0.25 g) crystallized, recrystallization from the same solvent gave the pure dicarboxylic acid, m.p. 104–107° C undepressed when mixed with authentic azelaic acid. After removing the ethyl acetate the remaining acids were converted to the *n*-butyl esters by 4 hours' reflux with excess *n*-butanol containing 4% HCl. The butyl 8-hydroxypelargonate was separated from the dibutyl azelate by gas chromatography of 100-mg batches using 1:6 silicone on Celite (60–80 mesh) in a 6 ft×¼ in. copper column. The apparatus was operated at 200° C with injector at 225° C, and a flow rate of 75 ml of helium per minute. The *n*-butyl 8-hydroxypelargonate was distilled, b.p./0.05 mm 115° C (bath). Calculated for $C_{13}H_{26}O_3$: C, 67.8%; H, 11.4%. Found: C, 67.2%; H, 11.3%; $[\alpha]_D$ +4.8° (*c*, 6.8, MeOH). Alkaline hydrolysis of this ester yielded 8-hydroxypelargonic acid as a colorless syrup, b.p./0.04 mm 110° C (bath); $[\alpha]_D$ +6.7° (*c*, 10.1, MeOH). Calculated for $C_9H_{18}O_3$: C, 62.0%; H, 10.4%. Found: C, 62.1%; H, 10.3%. Oxidation of the acid with chromic oxide in the same way as for 17-hydroxystearic acid gave 8-oxopelargonic acid, m.p. 41–42° C (lit. (9) gives m.p. 40–41° C). Calculated for $C_9H_{16}O_3$: C, 62.8%; H, 9.4%. Found: C, 62.9%; H, 9.4%. The semicarbazone crystallized from aqueous methanol and had a melting point of 136.5–138.5° C (lit. (10) gives m.p. 136° C).

Hydroxylation of the Solid Glycolipid Mixture (I and II)

The mixed glycosides (44 g) were dissolved in formic acid (120 cc) and then 30% hydrogen peroxide (10 cc) added. After storage at 0° C for 18 hours the solution was evaporated to a dry crust which was then dissolved in refluxing methanol (1 l.). Sodium metal was added until the solution became alkaline and after 30 minutes the solvent was removed by evaporation. The solid was then dissolved in water and cations removed by shaking with Amberlite IR-120. Precipitation of glycosides on the resin took place, but redissolution was effected by adding an excess of methanol. Filtration and evaporation afforded a crusty light-yellow solid (39.5 g) containing unaffected glycoside and its *threo*-dihydroxy counterparts.

The amount of olefin in the original glycoside mixture was then estimated by lead tetraacetate oxidation of the hydroxylated product. The solid (100 mg) was dissolved in acetic acid (5 cc) and to this solution 1% lead tetraacetate (10 cc) was added. The uptake of oxidant after 3, 10, and 25 minutes corresponded to oxidation equivalents, based on 1 molar uptake of lead tetraacetate, of 2260, 2140, and 1940 respectively indicating 30% of olefinic glycoside.

Isolation of 17-Hydroxyoctadecanoic Acid β-Sophoroside, 1,8-Nonanediol β-Sophoroside, and ω-Hydroxypelargonic Acid

The mixed dihydroxy- and unhydroxylated 17-hydroxy-octadecanoic acid sophorosides (23 g) containing 30% of the former was dissolved in acetic acid (250 cc). Lead tetraacetate (13 mM.) in acetic acid (500 cc) was added and after 30 minutes oxalic acid dihydrate (13 mM.) in acetic acid (50 cc) was added and the precipitate filtered off. Evaporation to a residue and addition of water gave a solution from which 17-hydroxyoctadecanoic acid β-sophoroside precipitated. This material was isolated, dried, and boiled in ether to remove fatty acid fragments. It (11.1 g) had a melting point of 139–140° C and $[\alpha]_D$ −22° (*c*, 1.3, aqueous $NaHCO_3$). Calculated for $C_{30}H_{56}O_{13}$: C, 57.6%; H, 9.0%; sap. equiv., 624. Found: C, 57.7%; H, 9.0%; sap. equiv., 566; neutral equiv., 1050. The product was methanolyzed with 4% methanolic hydrogen chloride overnight under reflux. The methyl ester, obtained by neutralization (Ag_2CO_3), filtration, and evaporation, consisted mainly of the C_{18} ester with traces of other hydroxy methyl esters as shown by gas – liquid phase chromatography.

The mother liquor of the above glycoside precipitation was evaporated to a syrup and reduced with sodium borohydride (1.0 g) in water (100 cc). After 1 hour excess reductant was destroyed with acetic acid, cations removed with Amberlite IR-120, and the resulting filtrate evaporated to a crust. Boric acid was removed by repeated evaporation of the solid with methanol to give nonanediol β-sophoroside, which was recrystallized twice from ethanol to give material (3.2 g) with m.p. 188–190° C and $[\alpha]_D$ −30° (*c*, 1.0, H_2O). Calculated for $C_{21}H_{40}O_{12}$: C, 52.1%; H, 8.3%. Found: C, 51.9%; H, 8.3%.

In order to characterize the other fission fragment of the olefin 858 mg of the mixed hydroxylated glycosides was oxidized with lead tetraacetate in a similar manner to that described above, except that after filtration of the lead oxalate the filtrate was evaporated to a syrup to which sodium borohydride (250 mg) in water (25 cc) was added. After 1 hour the mixture was worked up and the product extracted with boiling ether to give a syrup (0.13 g) which crystallized. Two recrystallizations from ether afforded ω-hydroxypelargonic acid, m.p. and mixed m.p. 48–50° C. Calculated for $C_9H_{18}O_3$: C, 62.0%; H, 10.4%. Found: C, 62.1%; H, 10.1%. The material not extractable by ether was dissolved in methanol and precipitated by addition of excess water. Filtration

afforded a powder which gave on methanolysis (4% MeOH–HCl under reflux overnight) mainly two ether-soluble compounds corresponding to a C_{18} hydroxy methyl ester and an octadecanediol (by G.L.P.C.) thus indicating that reduction of a lactone had taken place.

Hydrolysis of 1,8-Nonanediol Sophoroside

The sophoroside (296 mg) was hydrolyzed by heating on a steam bath for 18 hours in *N* sulphuric acid (5 cc). The solution was neutralized ($BaCO_3$), filtered, and evaporated to a syrup which was extracted with boiling ether. Evaporation of the ether afforded the nonanediol (85 mg) with $[\alpha]_D$ +6.5° (*c*, 2.3, H_2O) and 40 mg of this was dissolved in pyridine (2 cc) containing *p*-nitrobenzoyl chloride (300 mg), and kept at 80° C for 30 minutes. To this an excess of aqueous sodium bicarbonate was added and after shaking for 2 hours the precipitate was collected, washed, and dried, and twice recrystallized from ethyl acetate – hexane. The 1,8-nonanediol bis-*p*-nitrobenzoate (93 mg) had a melting point of 94–96° C and $[\alpha]_D$ +21° (*c*, 2.1, $CHCl_3$). Calculated for $C_{23}H_{26}O_8N_2$: C, 60.3%; H, 5.7%; N, 6.1%. Found: C, 60.4%; H, 5.7%; N, 6.1%.

The residual glucose (233 mg) was crystallized from methanol to give crystals (168 mg) with m.p. and mixed m.p. 146–149° C.

Partial Hydrolysis of 1,8-Nonanediol Sophoroside

Nonanediol sophoroside (2.0 g) was partially hydrolyzed by keeping a solution in *N* sulphuric acid (10 cc) for 4 hours at 75° C. After neutralization ($BaCO_3$), filtration, and evaporation the residual syrup was chromatographed on a cellulose column using *n*-butanol one-half saturated with water as the mobile phase. The solvent eluted firstly 1,8-nonanediol β-D-glucopyranoside (396 mg), which was recrystallized twice from ethyl acetate to give material with m.p. 102–104° C and $[\alpha]_D$ −27° (*c*, 1.8, H_2O). Calculated for $C_{15}H_{30}O_7$: C, 55.9%; H, 9.4%. Found: C, 55.7%; H, 9.4%. This was followed by unhydrolyzed glycoside (670 mg) and glucose (396 mg), which were not positively identified. *n*-Butanol – ethanol – water (4:1:1 v/v) was then passed through the column to elute sophorose (163 mg), which after two crystallizations from methanol–ethanol, gave 80 mg of the α-anomer with m.p. 198–202° C (25) and $[\alpha]_D$ +27° → 19° (*c*, 0.9, H_2O; constant, 42 hours). Calculated for $C_{12}H_{22}O_{11}$: C, 42.1%; H, 6.5%. Found: C, 41.9%; H, 6.5%. Acetylation of the disaccharide gave the β-octaacetate with m.p. 192–195° C (25).

Methylation of 1,8-Nonanediol β-Sophoroside

Nonanediol sophoroside (647 mg) was methylated six times by the dimethyl sulphate – aqueous sodium hydroxide method (26). At the end of the methylation excess reagent was destroyed by heating the solution on a steam bath for 3 hours. It was then cooled and neutralized with aqueous sulphuric acid and then shaken three times with chloroform. The extract was dried ($MgSO_4$), filtered, and evaporated to a syrup (754 mg) which was methylated further with silver oxide – methyl iodide under reflux (27). The methylated product (623 mg) had —OCH_3: 39.1% (calculated for $C_{21}H_{32}O_4(OCH_3)_8$: OCH_3, 41.6%), n_D^{27} 1.4583 and $[\alpha]_D$ −4° (*c*, 2.6, hexane).

The fully methylated glycoside was refluxed overnight in 4% methanolic hydrogen chloride (20 cc) and then *N* hydrochloric acid (10 cc) was added and the methanolic component boiled off. After 20 hours heating on a steam bath the solution was shaken with hexane to remove 1-methoxy-8-nonanol (57 mg), which had n_D^{24} 1.4410 and $[\alpha]_D$ +8° (*c*, 1.9, hexane) after vacuum distillation. The aqueous portion was neutralized (Ag_2CO_3), filtered, and taken down to a syrup (443 mg) which was chromatographed

on cellulose using benzene–ethanol–water (500:50:1 v/v) as solvent. 2,3,4,6-Tetra-*O*-methyl-D-glucose (164 mg) was eluted and recrystallized twice from hexane to give crystals, m.p. and mixed m.p. 80–81° C. Calculated for $C_6H_8O_2(OCH_3)_4$: OCH_3, 51.6%. Found: OCH_3, 51.4%. 3,4,6-Tri-*O*-methyl-D-glucose (144 mg) (28) came off later and two recrystallizations from ether–hexane gave 37 mg of product with m.p. 77–79° C and $[\alpha]_D$ +107° (3 minutes) → 75° (*c*, 0.9, H_2O; 16 hours, constant value). Calculated for $C_6H_9O_3(OCH_3)_3$: OCH_3, 41.9%. Found: OCH_3, 41.4%. On treatment with 1% lead tetraacetate in acetic acid (0.9 molar equivalents) the sugar consumed 0.24, 0.47, and 0.68 molar equivalents of oxidant after 3, 10, and 25 minutes respectively, thus indicating that the 1 and 2 positions of the sugar are not substituted with methoxyl groups (29).

Methylation of 17-Hydroxyoctadecanoic Acid β-Sophoroside

The glycoside (2 g) was methylated with dimethyl sulphate – sodium hydroxide and Purdie's reagent as described for the nonanediol sophoroside. The fully methylated product (1.94 g) n_D^{25} 1.4620 had OCH_3, 32.9%. Calculated for $C_{30}H_{28}O_5(OCH_3)_8$: OCH_3, 33.7%. The fully methylated glycoside was also hydrolyzed under similar conditions and the insoluble residue which accumulated was washed with water and hydrolyzed for 2 hours in 50% aqueous ethanol (20 cc) containing sodium hydroxide (0.5 g). The solution was added to excess water which was acidified (dil. H_2SO_4) and extracted with ether which was dried ($MgSO_4$), filtered, and evaporated to a solid (767 mg). Two recrystallizations from acetone gave 310 mg of 17-hydroxyoctadecanoic acid with m.p. 77–79° C and $[\alpha]_D$ +4.3° (*c*, 10.4, acetic acid). Calculated for $C_{18}H_{36}O_3$: C, 71.9%; H, 12.1%. Found: C, 71.6%; H, 12.0%. Two further recrystallizations from acetone elevated the melting point to 80.5–82° C (constant m.p.).

The aqueous portion of the hydrolyzate was neutralized and chromatographed on a cellulose column as described for the previous methylation. The products consisted of 2,3,4,6-tetra-*O*-methyl-D-glucose (0.43 g), which was crystallized twice from hexane to give a product, m.p. and mixed m.p. 79–80° C, and 3,4,6-tri-*O*-methyl-D-glucose (0.30 g), m.p. and mixed m.p. 77–80° C (two recrystallizations from ether – *n*-hexane).

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DEUTERATION OF FLUORENE AT C_9 AND THE ASSIGNMENT OF CERTAIN BANDS IN THE INFRARED SPECTRUM TO THE $>CDH$ AND $>CD_2$ GROUPS[1]

G. W. H. Scherf and R. K. Brown

ABSTRACT

Equimolar amounts of 9-fluorenylpotassium and deuterium oxide, or potassium deuteroxide and fluorene, or potassium hydroxide, fluorene, and deuterium oxide gave a mixture of unchanged fluorene, 9-deuterofluorene, and 9,9-dideuterofluorene. In 1,2-dimethoxyethane (DME) deuteration occurs more readily and dideuteration is more extensive than in dioxane. Lithium deuteroxide and fluorene in DME show no exchange, but upon addition of deuterium oxide some monodeuteration occurs. 9-Fluorenyllithium and deuterium oxide in DME gives as much as 80% of 9-deuterofluorene accompanied by a small amount of dideuteration. Dideuteration is practically eliminated, and monodeuteration correspondingly increased when the same reaction is carried out in hexane.

The bands at 667 cm^{-1}, 827 cm^{-1}, and 974 cm^{-1} have been assigned definitely to the $>CD_2$ group while those at 677 cm^{-1} and 832 cm^{-1} are due to the $>CDH$ group in fluorene.

Recently six absorption bands in the infrared spectrum of fluorene have been assigned to the $>CH_2$ group of that molecule (1). Evidence for such assignment was obtained from the study of the spectra of C_9-mono- and -di-alkylated as well as C_9-mono- and -di-deuterated fluorene. Mono- or di-deuteration at C_9 reduced or eliminated the absorption at the frequencies designated but in turn produced new bands at lower frequencies in the positions expected when a deuterium atom replaces an hydrogen atom attached to carbon (2). The new frequencies associated with the C_9—D bond were located at least tentatively, if not definitely, at 2150, 974, 939, 827, and 667 cm^{-1}, respectively. In addition, a band at 677 cm^{-1} was thought to be due to a vibration of the remaining C_9—H group in the monodeuterated molecule but shifted slightly from its normal frequency of

$$\begin{array}{c} | \\ \text{DC—H} \\ | \end{array}$$

692 cm^{-1} by the presence of the deuterium atom (i.e. DC—H). Also, the band at 939 cm^{-1} was believed to contain a contribution due to the same structural feature.

For the work mentioned above, the 9-deuterofluorene was made by the reaction of excess deuterium oxide with 9-fluorenylpotassium in dioxane at room temperature. The 9,9-dideuterofluorene was prepared by similar addition of excess deuterium oxide to the substance formed when two equivalents of potassium metal reacted with one of fluorene in dioxane (1).

During a more detailed study of the preparation of 9-fluorenylpotassium in various solvents (3) the measurement of the extent of metalation by means of deuterating the organometallic compound (particularly with excess deuterium oxide) was shown to be questionable. It was observed that equimolar quantities of potassium deuteroxide and fluorene in dioxane, under anhydrous conditions, when kept at room temperature for 1 hour, gave 10 to 15% C_9-deuteration while equimolar amounts of potassium hydroxide,

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Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta. Taken from the thesis of G. W. H. Scherf to be submitted to the Graduate School of the University of Alberta in partial fulfillment of the requirements for the Degree of Doctor of Philosophy.

fluorene, and deuterium oxide in dioxane at room temperature for 3 hours produced 5 to 8% C_9-deuteration.

In addition the "9-deuterofluorene" previously prepared was shown to be contaminated with a trace of fluorene and a larger amount of 9,9-dideuterofluorene attributed to exchange due to the presence of potassium deuteroxide and excess deuterium oxide (1). From the tentative assignment of the 677 cm^{-1} and 667 cm^{-1} bands to the structural group DC—H and HC—D, respectively, both these bands should appear in the spectrum of 9-deuterofluorene. However, in the spectrum of 9,9-dideuterofluorene the 677 cm^{-1} band should be absent and the band at 667 cm^{-1} should double its intensity. As actually observed from the spectra of the mono- and di-deuterated fluorenes (Figs. 2 and 3, ref. 1) the 677 cm^{-1} band did nearly vanish while that at 667 cm^{-1} increased considerably, although not to twice its original magnitude. From this information, along with data from N.M.R. analyses of the "9-deuterofluorene", the purity of the monodeuterated compound had been estimated to be about 75%, the bulk of the remainder being the dideuterated material. This was in keeping with the greater area of the 667 cm^{-1} band. Although the N.M.R. spectrum could be interpreted as containing a somewhat greater proportion of the dideuterated fluorene than stated above, the broad but low signal was sufficient to agree fairly well with the above assignments in the infrared. An implicit assumption in this reasoning is that the 677 cm^{-1} and 667 cm^{-1} bands due respectively to the DC—H and HC—D are of about equal intensity for equal concentrations.

Support or modifications of the interpretations outlined above would be gained from the preparation and examination of authentic C_9-monodeuterated fluorene, uncontaminated as much as possible by fluorene and especially by 9,9-dideuterofluorene.

This paper presents results of the study of C_9-mono- and -di-deuteration of fluorene and gives the exact assignment of certain bands in the infrared associated with 9-mono- and 9,9-di-deuterofluorene.

RESULTS AND DISCUSSION

Since 9-fluorenyllithium, prepared by the reaction of fluorene with lithium (or lithium amide) preferably in ethers of ethylene glycol (4), produced essentially C_9-monosubstituted fluorene when treated with an equivalent amount of alkyl halide (5), the lithium salt was thought to be the most promising substance for the production of 9-deuterofluorene. The addition of deuterium oxide to an equimolar portion of 9-fluorenyllithium prepared in 1,2-dimethoxyethane (DME) (4) gave a product whose spectrum is shown in Fig. 1. It is clearly seen that a strong band appears at 677 cm^{-1} while the one at 667 cm^{-1} is quite small. The bands at 692 cm^{-1}, 952 cm^{-1}, and 1400 cm^{-1} show that there is some unchanged fluorene present, roughly to the extent of 12%. The N.M.R. analysis of this compound* shows a signal for the proton at C_9 (Fig. 2*a*) which is nearly half that found for the proton at C_9 of the parent fluorene (Fig. 2*b*). The broadening of the signal in Fig. 2*a* is probably due to spin coupling of the proton with the deuterium atom. Both the infrared and N.M.R. spectra are in agreement with the interpretation that the substance contains a high percentage of 9-deuterofluorene. The band at 677 cm^{-1} is thus due to the group $\rangle$CDH while that at 667 cm^{-1} arises from the structural feature $\rangle CD_2$. The

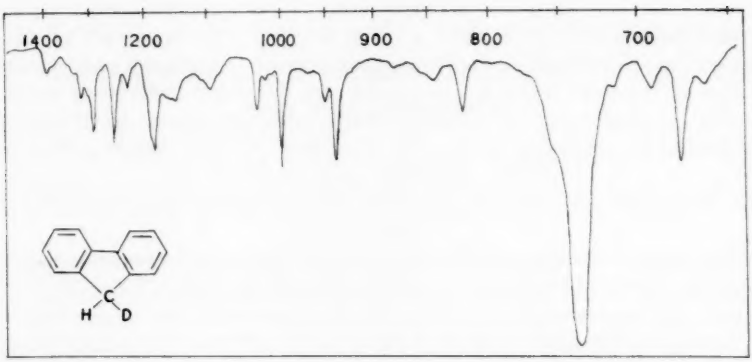


FIG. 1. I. R. spectrum in CS_2 of 9-deuterofluorene prepared from 9-fluorenyllithium and D_2O in 1,2-dimethoxyethane.

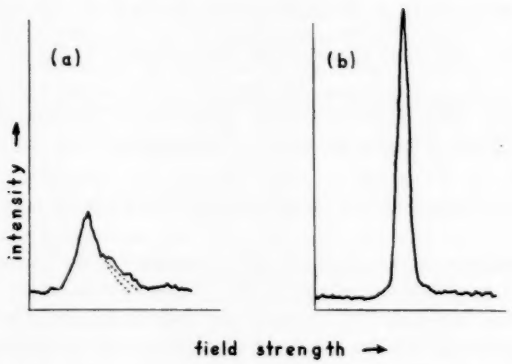


FIG. 2. Partial N.M.R. spectra showing only $\rangle$CHD and $\rangle CH_2$ bands of fluorene. (*a*) 9-Deuterofluorene. (*b*) Fluorene. The 9-deuterofluorene was prepared from 9-fluorenyllithium + D_2O in 1,2-dimethoxyethane.

product, described in the first paper of this series (1) and obtained from the reaction of 9-fluorenylpotassium with excess deuterium oxide in dioxane, therefore must have been composed of a mixture of C_9-mono- and -di-deuterated fluorene in the approximate ratio of 2 to 3. This mixture clearly contained a small amount of unchanged fluorene as a contaminant (Fig. 2, ref. 1).

Comparison of the spectrum of the 80% monodeuterated fluorene (Fig. 1, this paper) with that of the mixture of C_9-mono- and C_9-di-deuterated fluorene (Fig. 2, ref. 1) and 9,9-dideuterated fluorene (Fig. 3, ref. 1) shows that the band at 827 cm^{-1} is due to $\rangle CD_2$ while that at 823 cm^{-1} arises from the group $\rangle$CDH. The 974 cm^{-1} band, which appears much more clearly in the 9,9-dideuterofluorene and is nearly absent in the 80% 9-deuterofluorene, must then also be due to the structure $\rangle CD_2$ rather than to $\rangle$CDH. The band at 939 cm^{-1} appears in both C_9-mono- and C_9-di-deuterofluorene and is due to the carbon–deuterium bond in both $\rangle CD_2$ and $\rangle$CDH.

With the knowledge of the exact assignment of these bands due to $\rangle CD_2$, $\rangle CDH$, and $\rangle CH_2$ now available, some experiments on the deuteration of fluorene were carried out. The mixtures, conditions of reaction, and results are presented in Table I. The

TABLE I

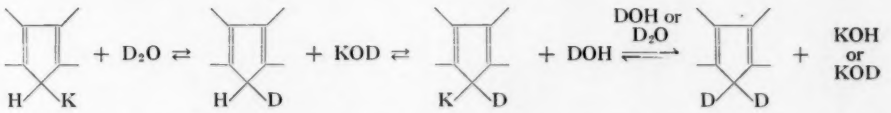
Mono- and di-deuteration of fluorene
(Except where specified equivalent amounts of reagents were refluxed in 5 ml of solvent for 1 hour. DME = 1,2 dimethoxyethane)

Reagents	Solvent and conditions	% C_9H_2	% C_9DH	% C_9D_2
9-Fluorenylpotassium + D_2O (excess)*	Dioxane (room temperature, 1 hour)	2	38	60
9-Fluorenylpotassium + D_2O	Dioxane	35	50	15
9-Fluorenylpotassium + D_2O	DME	15	45	40
9-Fluorenylsodium + D_2O	DME	5	45	50
9-Fluorenyllithium + D_2O	Dioxane and trace DME	20	70	10
9-Fluorenyllithium + D_2O	DME	12	80	8
KOD + fluorene + D_2O	Dioxane (all KOD dissolved)	15	45	40
KOD + fluorene + D_2O†	DME (all KOD dissolved)	20	50	30
KOH + fluorene + D_2O	Dioxane (all KOH dissolved)	90	10	0
KOH + fluorene + D_2O	DME (all KOH dissolved)	45	50	5
KOD + fluorene	Dioxane (KOD not dissolved)	70	30	0
KOD + fluorene	DME (KOD not dissolved)	45	50	5
LiOD + fluorene‡	DME (LiOD not dissolved)	100	0	0
LiOD + fluorene + D_2O	DME (LiOD not dissolved)	90	10	0
LiOD + fluorene + D_2O (3-fold excess)	DME (LiOD not dissolved)	85	15	0
9-Fluorenyllithium§ and D_2O	Hexane	8	90	2

*From Fig. 2, ref. 1.
†The red color of 9-fluorenylpotassium became evident within the first 3 minutes.
‡Repeated twice with same results.
§Made in DEE (4), isolated, and transferred to hexane.

yields of mono- and di-deuterated fluorene, and unchanged fluorene were estimated from the magnitude of the bands at 677 cm^{-1}, 667 cm^{-1}, and 692 (or 952) cm^{-1}, 667 cm^{-1}, and 692 (or 952) cm^{-1}, respectively.

It is clearly seen that 9-fluorenylpotassium, when treated with an equimolar amount of deuterium oxide, produced less unchanged fluorene and more dideuteration in DME than in dioxane. Such deuteration no doubt occurred via the sequence shown below:



Unchanged fluorene might have come from (*a*) incomplete metalation, (*b*) a small amount of water in the deuterium oxide, (*c*) a combination of 9-fluorenylpotassium with the water or deuterium hydroxide produced in the first part of the reaction. The more extensive dideuteration which occurred in the solvent DME agrees with the greater effectiveness of DME as a solvent in the preparation and reactions of 9-fluorenylpotassium (4, 5) due to the more effective solvation of the ether with potassium deuteroxide, enhancing the latter's basicity.

9-Fluorenyllithium in DME, on the other hand, gave largely C_9-*mono*deuteration accompanied by only a small proportion of dideuterated and unchanged fluorene. But with the solvent hexane rather than DME, dideuteration was practically eliminated and the extent of monodeuteration increased correspondingly (Fig. 3).

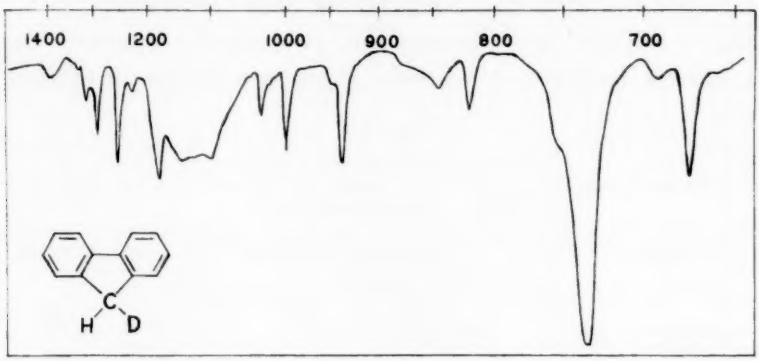


FIG. 3. I. R. spectrum in CS_2 of 9-deuterofluorene prepared from 9-fluorenyllithium and D_2O in hexane.

Potassium deuteroxide and fluorene in dioxane gave more extensive dideuteration than did a mixture of potassium hydroxide, fluorene, and deuterium oxide, in dioxane. This is probably due to the fact that in the reaction of potassium deuteroxide with fluorene, the products of the first step in the exchange,

+ HOD, are in close proximity, thus facilitating the next step of exchange, whereas the product of the reaction of potassium hydroxide and fluorene requires time for collision with the solvated deuterium oxide. With DME as solvent, such differences appear to be minimized.

Lithium deuteroxide and fluorene failed to show any exchange, but when deuterium oxide was added, exchange did occur and increased in magnitude with the amount of deuterium oxide added. This agrees with the interpretation that lithium deuteroxide under anhydrous conditions is a much weaker base than is either potassium deuteroxide or sodium deuteroxide and hence will not initiate the first step of the reaction—that of transient formation of the 9-fluorenyllithium. The addition of deuterium oxide yields a solvent which promotes the ionization of lithium deuteroxide and enhances its basicity. Such a levelling effect of solvents has been observed before (6).

EXPERIMENTAL

The 9-fluorenyl-potassium, -sodium, and -lithium were made according to previous directions (1, 4).

Preparation of Potassium Deuteroxide and Lithium Deuteroxide

Into 100 ml of dry hexane was pipetted 1 ml of 98% D_2O. A piece of freshly cut potassium in excess of the amount required to react with all the D_2O was suspended on a length of wire and immersed in the hexane and cautiously allowed to touch the surface of the D_2O at the bottom of the flask and then was immediately withdrawn but not removed from the hexane. This "dipping" process was repeated until a coating of KOD was developed on the surface of the metal. The reaction was quite vigorous at first but soon moderated. The solid was allowed to remain overnight in the flask in contact with the

small amount of D_2O in the lower layer. The KOD was then removed from the metal and, following the elimination of hexane, was weighed for use.

LiOD was prepared by a similar manner but required somewhat longer contact with the traces of D_2O for complete reaction.

Deuteration Experiments

All reactions were carried out under the same conditions. A typical reaction is described.

Equimolar amounts of the reagents, KOD, fluorene, and D_2O (0.01 mole of each) were allowed to react for 1 hour in 5 ml of refluxing solvent. An atmosphere of pure, dry nitrogen was maintained throughout. The cooled solution was then treated with a mixture of ether and water. The ether extract, dried over calcium chloride, was freed from solvent and the solid crystallized from alcohol.

ACKNOWLEDGMENTS

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CONTRIBUTION À L'ÉTUDE DE LA RÉACTION DE VON RICHTER

IV. COMMENTAIRES CONCERNANT LA RÉACTION[1]

E. CULLEN[2] ET PH. L'ÉCUYER

RÉSUMÉ

Il existe une relation entre l'anhydride carbonique et les composés azoxyques formés au cours de la réaction. Ces composés azoxyques, dans la série du benzène, ne donnent pas les acides benzoïques attendus, lorsqu'ils sont soumis aux conditions de la réaction. Par contre, dans la série du naphtalène, les composés qui ont été isolés et dont la formule empirique correspond aux composés azoxyques attendus se transforment en acides naphtoïques. Enfin, le 2-nitro-5-chlorobenzonitrile ne produit pas de composé azoxyque, ni d'acide *m*-chlorobenzoïque.

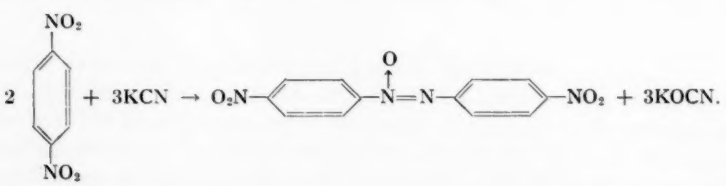
Durant la réaction de von Richter,[3] il se forme de l'ammoniac. Celui-ci peut provenir de l'hydrolyse de la fonction nitrile qui se fixe à l'anneau benzénique et d'une certaine quantité de cyanure ou de cyanate de potassium. L'hydrolyse du cyanure de potassium (*a*) est, toutefois, extrêmement lente à la température d'ébullition. Nous avons constaté que seulement 7% du cyanure s'hydrolyse en acide formique et en ammoniac, lorsqu'on fait bouillir à reflux pendant 48 heures une solution de cyanure de potassium dans l'éthanol à 50%.

$$KCN + 2H_2O \rightarrow HCO_2K + NH_3 \qquad (a)$$

En milieu aqueux, le cyanure de potassium s'oxyde en cyanate aux dépens d'un groupe nitré (1) et le cyanate s'hydrolyse ensuite en ammoniac et bicarbonate de potassium (*b*). Ainsi, dans la réduction du *p*-dinitrobenzène en 4,4′-dinitroazoxybenzène, le rendement du composé azoxyque est proportionnel à la quantité de cyanate qui se forme durant la réaction. Cependant en solution alcoolique, le rendement du composé azoxyque est beaucoup plus faible, le groupe nitré étant en majeure partie substitué par la fonction oxalcoyle. Durant la réaction de von Richter dans l'éthanol à 50%, il se forme aussi de l'anhydride carbonique. Nous l'avons dosé pour nous rendre compte de la proportion de la substance nitrée de départ qui est réduite de cette façon.

$$KCN \xrightarrow{[O]} KOCN \xrightarrow{2H_2O} NH_3 + KHCO_3 \qquad (b)$$

Après 4 heures d'ébullition à reflux dans le 2-éthoxyéthanol à 50%, il s'est formé pour 1 mole de *p*-chloronitrobenzène, 0.148 mole de gaz carbonique et 0.031 mole de 3,8-dichloro-6-iminoquinazolo[1,2,2′,3′]indazol (III) (2). D'après la quantité d'anhydride carbonique dégagé, il aurait dû théoriquement s'être formé 0.049 mole du composé azoxyque II, si on se réfère à (*c*):



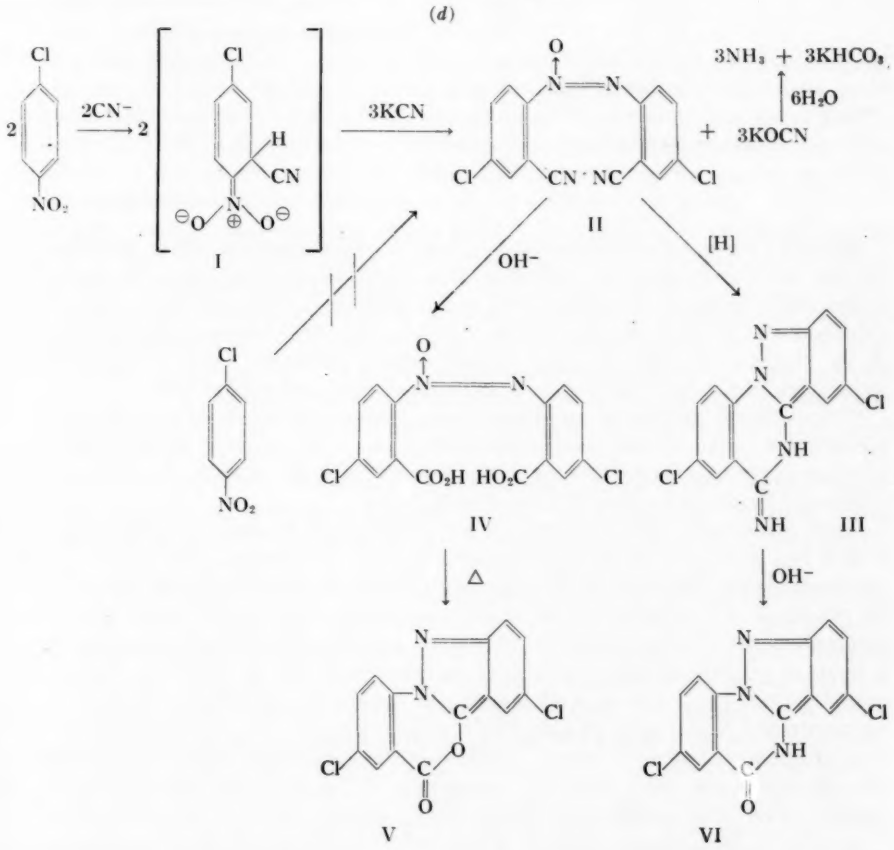
(*c*)

[1]*Manuscrit reçu le 11 octobre 1960.*
Contribution du Département de Chimie, Faculté des Sciences, Université Laval, Québec, Qué.
[2]*Bénéficiaire de bourses d'études accordées par le Conseil national de Recherches du Canada, les firmes C.I.L. et Shell Oil et l'Office de Recherches scientifiques de la Province de Québec.*
[3]*Consulter la référence 3 pour la bibliographie des mémoires antérieurs concernant cette réaction.*

La différence de 0.018 mole peut provenir d'une part, de l'hydrolyse d'une certaine quantité du composé azoxyque II en l'acide correspondant IV, qui par sublimation se transforme en la lactone de l'acide 5-chloro-2-[5-chloro-3-oxy-indazyl-(2)]-benzoïque (V), et d'autre part, de l'hydrolyse partielle du produit neutre III en 3,8-dichloro-6-cétoquinazolo[1,2,2′,3′]indazol (VI) (3).

La formation de la substance neutre III qui dépend de celle du 4,4′-dichloro-2,2′-dicyanoazoxybenzène (II) (ou du dicarbamyle correspondant), est ainsi, d'après les résultats précédents, indirectement reliée à celle du cyanate et partant de l'anhydride carbonique (*d*).

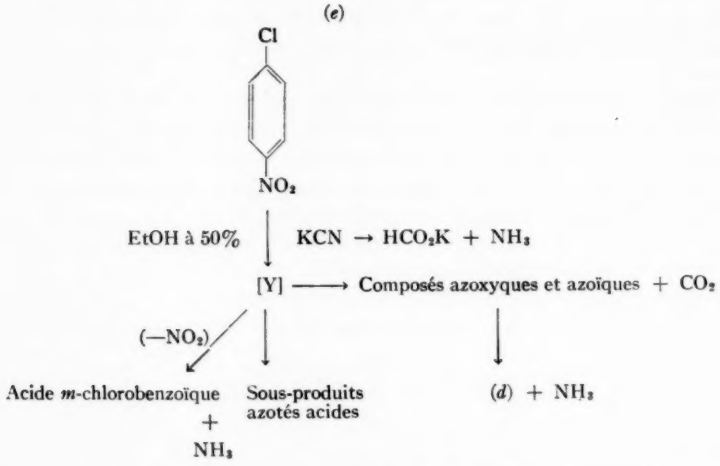
Nous avons aussi dosé l'ammoniac qui se dégage au cours de la réaction du *p*-chloronitrobenzène avec le cyanure de potassium dans l'éthanol à 50% ou le 2-éthoxyéthanol à 50%. Dans l'un ou l'autre solvant, la quantité d'ammoniac dégagé correspond à environ 75% de la substance nitrée de départ, les corrections étant faites pour l'apport de l'ammoniac attribuable aux réactions secondaires (*a*) et (*b*).



Ces réactions secondaires enlèvent à la réaction de von Richter toute valeur synthétique, parce qu'une réaction d'oxydo–réduction entre le groupe nitré et le cyanure de potassium

accompagne la fixation du groupement nitrile au noyau aromatique. En nous basant sur les observations précédentes et d'autres faites jusqu'ici concernant cette réaction, nous pouvons déduire que celle-ci, en plus de donner naissance à un acide dans lequel le groupe nitré est éliminé, engendre divers composés azotés plus ou moins réduits selon les transformations indiquées en (*e*), Y représentant un intermédiaire.

(*e*)



Excepté l'acide 4,4′-dichloroazoxybenzène-2,2′-dicarboxylique qui se transforme en la lactone de l'acide 5-chloro-2-[5-chloro-3-oxy-indazyl-(2)]-benzoïque, les sous-produits acides (80% du total) ne se subliment pas. Ceci porte à croire que la majeure partie des substances à caractère acide qui accompagnent l'acide *m*-chlorobenzoïque dans le produit de la réaction ne sont pas des dérivés réduits azoïques, azoxyques, hydrazoïques, indazylbenzoïques ou anthraniliques; car ceux-ci sont tous sublimables.

Dans le but d'observer si un intermédiaire s'accumule durant la réaction, nous avons déterminé la quantité des principales substances qui se trouvent dans le produit de la réaction après une ébullition plus ou moins prolongée des réactifs. Nous présentons au Tableau I les résultats de cette série d'expériences.

Après 2 heures d'ébullition à reflux d'une solution de 0.01 mole de *p*-chloronitrobenzène et de 0.1 mole de cyanure de potassium dans le tétrahydrofurfurol à 50%, tout le *p*-chloronitrobenzène est disparu et le poids des acides bruts ne varie plus, quel que soit le temps de chauffage. Cependant, l'acide *m*-chlorobenzoïque continue de se former lentement pendant encore plusieurs heures au détriment, semble-t-il, des autres produits acides, car le poids de ces derniers diminue proportionnellement à celui de l'acide *m*-chlorobenzoïque qui se forme. De 2 heures à 48 heures, le rendement de l'acide *m*-chlorobenzoïque augmente de 6% alors que celui du résidu acide diminue de 5%. Pendant le même temps, le pourcentage du produit neutre, le 3,8-dichloro-6-iminoquinazolo[1,2,2′,3′]indazol (V), décroît aussi après avoir atteint un maximum. C'est qu'il s'hydrolyse très lentement dans le milieu réactionnel en 3,8-dichloro-6-cétoquinazolo[1,2,2′,3′]indazol (VI) (2).

Rauhut et Bunnett ont observé qu'une solution alcoolique diluée de *m*-nitroanisole et de cyanure de sodium donne du 4,4′-diméthoxy-2,2′-dicarbamylazoxybenzène sans acide *m*-anisique, lorsqu'elle est bouillie à reflux (4), mais qu'elle produit 3% d'acide anisique en plus d'un composé neutre non-identifié, lorsqu'elle est chauffée en tube scellé,

TABLEAU I

Pourcentage des produits formés par la réaction du *p*-chloronitrobenzène et du cyanure de potassium dans le tétrahydrofurfurol à 50% en fonction du temps d'ébullition

Temps d'ébullition, heures	*p*-Chloro-nitrobenzène récupéré, %	Produits neutres		Produits acides		
		Bruts %	*k** %	Bruts %	Acide *m*-chloro-benzoïque	Résidu %
¼	45.5	2.0	—	20.2	3.0	17.2
½	29.1	12.0	1.6	38.0	8.0	30.0
¾	14.8	15.8	3.5	52.0	14.6	37.4
1	4.5	17.8	5.2	58.0	18.0	40.0
1½	3.5	14.2	4.5	58.0	20.0	38.0
2	0.0	15.0	4.5	70.0	22.0	48.0
4	0.0	13.0	—	70.0	24.0	46.0
8	0.0	11.5	3.6	70.8	25.0	45.0
24	0.0	—	—	—	29.0	—
48	0.0	9.0	2.6	71.0	28.0	43.0

*6-Iminoquinazolo[1,2,2′,3′]indazol.

à 180° (5). Ceci laisse supposer que le 4,4′-diméthoxy-2,2′-dicarbamylazoxybenzène peut se transformer en acide *m*-anisique en présence de cyanure de sodium; mais, nous avons vérifié que cela ne se produit dans l'éthanol aqueux, ni à l'ébullition dans le glycol à 50%, ni en tube scellé à 180°. Lorsqu'il est bouilli à reflux dans le méthanol avec de l'hydroxyde de potassium, le 4,4′-diméthoxy-2,2′-dicarbamylazoxybenzène se transforme en acide 4,4′-diméthoxybenzène-2,2′-dicarboxylique et non en acide *m*-anisique (4).

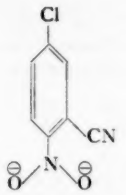
Soumis aux conditions de la réaction de von Richter, l'acide 4,4′-dichloroazoxybenzène-2,2′-dicarboxylique ne subit aucune transformation (5); le 2,2′-dicyanoazoxybenzène donne du 6-iminoquinazolo[1,2,2′,3′]indazol, mais non de l'acide benzoïque (2); le 2-nitro-4-chlorobenzonitrile ne fournit pas d'acide *p*-chlorobenzoïque (6) et nous avons constaté que l'acide 2-nitro-5-chlorobenzoïque, le 2-nitro-5-chlorobenzonitrile et la 2-nitro-5-chlorobenzamide n'engendrent ni l'acide *m*-chlorobenzoïque, ni aucun des produits azoxyques que fournit normalement la réaction. Ceux-ci sont donc formés au cours de la réaction par la réduction de l'intermédiaire dihydroaromatique I et non des substances aromatiques correspondantes (*d*).

Von Richter a proposé un mécanisme de la réaction (7), qui a été temporairement accepté par Bunnett et quelques collaborateurs (8). Ce mécanisme supposait qu'un intermédiaire dihydroaromatique (I) se transforme en nitrile par l'addition et l'élimination successive d'un proton, puis qu'il se produit le départ nucléofuge de l'ion nitrite.

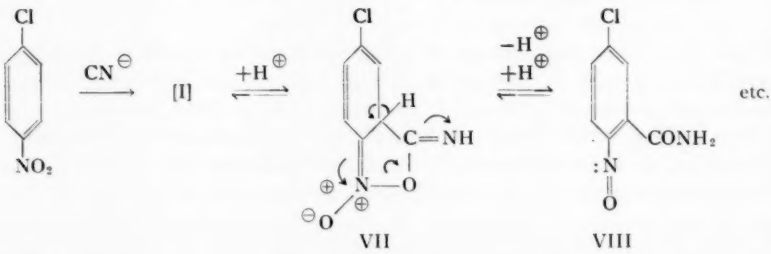
Bunnett et Rauhut (6) ont ensuite suggéré que l'élimination du groupement nitré sous forme de l'ion nitrite passe par l'intermédiaire d'un "imino-anhydride" (imino-isoxazoline) et d'un anhydride mixte de l'acide nitreux et de l'acide carboxylique. Dernièrement, Samuel (9) a observé que, lorsque la réaction est exécutée dans un solvant dont l'eau a été enrichie en isotope ^{18}O, l'acide carboxylique obtenu ne contient que la moitié de l'oxygène ^{18}O qu'il devrait posséder si les deux atomes d'oxygène du groupe carboxylique provenaient de l'eau. Il en conclut que l'un des atomes d'oxygène doit provenir du groupement nitré et que cela confirme le mécanisme proposé par Bunnett et Rauhut.

Tout récemment, après avoir constaté qu'il se trouve dans le produit de la réaction du *p*-chloronitrobenzène 50% d'azote et pas plus de 3% de l'ion nitrite qui devrait se former selon le mécanisme précédent, Rosenblum (10) a proposé une ingénieuse modification pour expliquer l'élimination de l'azote qui accompagnerait la formation de l'acide

m-chlorobenzoïque; mais néanmoins, il y a lieu de douter de l'existence de l'anion aromatique bivalent



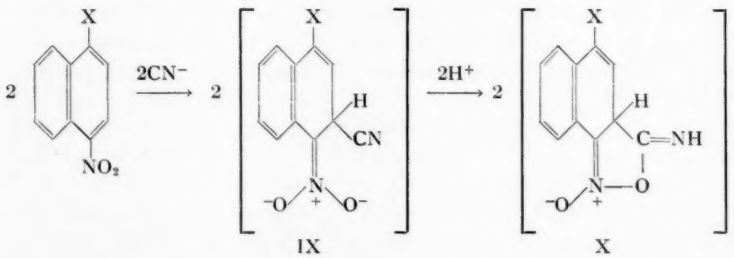
que cet auteur considère comme un intermédiaire de la réaction et qui n'est d'ailleurs pas nécessaire pour interpréter la formation du 4-nitroso-3-carbamylchlorobenzène (VIII), clef de ce nouveau mécanisme. En effet, nous sommes d'avis que la formation de l'intermédiaire VIII peut s'expliquer normalement par l'intermédiaire dihydroaromatique I des mécanismes précédents (6, 8, 9), de la façon suivante:



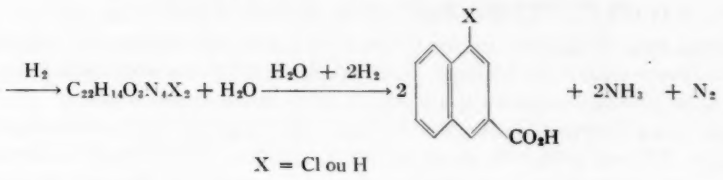
VII VIII

Quoi qu'il en soit, il est certain que dans la série du benzène, lorsque la substance nitrée est réduite en composés azoxyques ou azoïques, ces derniers ne peuvent pas se transformer en acides benzoïques dans les conditions de la réaction et ils sont isolés tels quels ou sous la forme de dérivés de l'indazol (2, 3). Par contre, dans la série du naphtalène, les substances, $C_{22}H_{14}O_3N_4Cl_2$ et $C_{22}H_{16}O_3N_2$, que nous avons respectivement isolées à la suite de réactions de von Richter avec le 4-chloro-1-nitronaphtalène et le nitronaphtalène suivant des conditions quelque peu modifiées, donnent naissance aux acides 4-chloro-2-naphtoïque et 2-naphtoïque (11), lorsqu'elles sont soumises aux conditions normales de la réaction.

À un atome d'oxygène près, la formule brute $C_{22}H_{14}O_3N_4X_2$ (X = H ou Cl) est le double de l'intermédiaire X, analogue à l'intermédiaire imino-anhydride proposé par Bunnett pour la réaction dans la série du benzène. Elle suppose l'union de deux molécules du dérivé nitré du naphtalène par réduction (*f*).



IX X (*f*)



X = Cl ou H

Si ces composés sont vraiment des intermédiaires de la réaction, il faudrait convenir que le mécanisme (du moins dans la série du naphtalène) fait intervenir un composé de réduction qui réunit deux molécules du produit de départ. Nous tentons présentement de trancher cette question.

PARTIE EXPÉRIMENTALE[4]

La réaction de von Richter a été exécutée en faisant bouillir à reflux une solution de *p*-nitrochlorobenzène et de cyanure de potassium.

Rendement en fonction du temps

On fait bouillir à reflux une solution comprenant une partie de *p*-nitrochlorobenzène et quatre parties de cyanure de potassium dans 10 parties de tétrahydrofurfurol à 50% (en volume). Au moment désiré, la réaction est interrompue. Les produits sont isolés et purifiés selon le mode opératoire déjà décrit (3). Les résultats sont présentés au Tableau I.

Dosage de l'anhydride carbonique

Du *p*-chloronitrobenzène (2.0 g), du cyanure de potassium (6.0 g) et du 2-éthoxyéthanol à 50% (30 ml) sont introduits dans un ballon de 100 ml à trois cols dont l'un est pourvu d'un réfrigérant, un autre d'un entonnoir à décantation et le troisième d'un tube de verre qui plonge dans le mélange réactionnel et peut être fermé à l'aide d'un robinet. Le mélange est bouilli à reflux pendant 4 heures, les robinets de l'entonnoir et du tube de verre étant fermés. Une fois la réaction terminée, après quelques minutes de repos à la température ambiante, on relie le réfrigérant à un flacon contenant 225 ml d'eau de baryte par un tube de verre qui plonge dans la solution de baryte. Tout en faisant barbotter un courant d'azote dans le mélange réactionnel, on y introduit, à l'aide de l'entonnoir, un excès d'acide chlorhydrique concentré suffisant pour rendre acide le produit de la réaction et on chauffe pour en chasser tout l'anhydride carbonique.

Le précipité de carbonate de baryum est filtré, lavé à l'eau, suspendu dans 50 ml d'eau, puis transformé en sulfate. Le précipité de sulfate de baryum est essoré, lavé par l'eau, séché et calciné. On obtient 0.4415 g de sulfate de baryum correspondant à 0.00189 mole (0.083 g) d'anhydride carbonique ou à 0.148 mole pour une mole de *p*-chloronitrobenzène. Dans une expérience témoin, sans *p*-chloronitrobenzène, il ne se forme pas d'anhydride carbonique.

Dosage de l'ammoniac

On introduit dans un ballon de 100 ml à deux tubulures, 2.0 g de *p*-chloronitrobenzène, 6.0 g de cyanure de potassium et 20 ml d'éthanol à 50%. L'un des cols du ballon est muni d'un tube de verre qui s'arrête au-dessus de la surface des réactifs et l'autre, d'un réfrigérant dont l'extrémité est reliée à un flacon laveur renversé et de là à une fiole conique par un tube qui plonge dans 100 ml d'acide chlorhydrique 0.5 *N*. On chauffe à

[4]*Les points de fusion ont été déterminés en tubes capillaires et ne sont pas corrigés.*

reflux pendant 47 heures et laisse ensuite reposer pendant quelques minutes à la température ambiante, tout en faisant circuler un courant d'azote dans l'appareil pour éviter les retours. On ajoute ensuite au mélange réactionnel, 10 ml d'une solution d'hydroxyde de potassium à 50% et fait bouillir de nouveau à reflux pendant une heure.

Pour neutraliser l'excès d'acide chlorhydrique 0.5 *N*, il faut 64.3 ml de soude 0.5 *N*. La différence, 35.7 ml (100−64.3), équivaut à 0.0179 mole (0.304 g) d'ammoniac ou 1.41 mole pour 1 mole de *p*-chloronitrobenzène. Une expérience témoin, en l'absence de *p*-chloronitrobenzène, a fourni 0.10845 g d'ammoniac. Ceci indique que 0.4301 g ou 7.18% du cyanure de potassium est hydrolysé durant la réaction.

Traitement de diverses substances dans les conditions de la réaction de von Richter

(a) 2,2'-Dicyanoazoxybenzène

À une solution de 9.0 g de 2-nitrobenzonitrile dans 75 ml d'acide acétique et 10 ml d'anhydride acétique on ajoute petit à petit (environ 1¼ heures) 12.0 g de zinc en poudre, sous agitation mécanique et en maintenant la température du mélange entre 30 et 35°. La pâte est ensuite versée dans 1 litre d'eau glacée et essorée. Le précipité est traité par 300 ml d'une solution de carbonate à 10% pendant 15 minutes à 40°, filtré et lavé à l'eau. Le solide est dissous dans de l'éthanol et la solution traitée au noir animal et filtrée. Le 2,2'-dicyanoazoxybenzène (3.9 g; 53% de la théorie) cristallise en fines aiguilles fondant à 192–193° (p.f. lit. 194° (12)).

Une solution de 1.0 g de 2,2'-dicyanoazoxybenzène et de 30 g de cyanure de potassium dans 200 ml de glycol d'éthylène aqueux (90%) est bouillie à reflux pendant 3 heures. Le produit de la réaction traité de la façon habituelle (2) a fourni 0.08 g de 6-iminoquinazolo-[1,2,2',3']indazol, mais pas d'acide benzoïque.

(b) 4,4'-Diméthoxy-2,2'-dicarbamylazoxybenzène

Le *p*-nitrophénol est méthylé, avec un rendement de 70% de la théorie, par le sulfate de méthyle, suivant les données d'Ullman (13) pour la méthylation de l'*o*-nitrophénol, et transformé en 4,4'-diméthoxy-2,2'-dicarbamylazoxybenzène (4). Ce dernier composé (1.0 g) se décompose, lorsqu'il est traité par la potasse (0.05 g) dans le glycol (10 ml) et ne réagit pas, en tube scellé à 150°, avec du cyanure de potassium (3.0 g) dans l'éthanol à 50% (10 ml).

(c) 2-Nitro-5-chlorobenzamide

De la 2-nitro-5-chlorobenzamide (3.5 g), obtenue à partir de l'acide 2-nitro-5-chlorobenzoïque préparé selon Bunnett (4), est bouillie à reflux pendant 24 heures avec 10.0 g de cyanure de potassium en solution dans 35 ml d'éthanol à 50%. Le produit de la réaction traité de la façon habituelle (2) ne fournit que des traces d'un produit acide qui n'est pas de l'acide *m*-chlorobenzoïque et un sublimé différent de la lactone de l'acide 5-chloro-2-[5-chloro-3-oxy-indazyl(2)]-benzoïque.

(d) 2-Nitro-5-chlorobenzonitrile

Du pentoxyde de phosphore (8.0 g) est intimement mélangé à de la 2-nitro-5-chlorobenzamide (4.0 g) et chauffé sous pression réduite. Le 2-nitro-5-chlorobenzonitrile distille à 120°/20 mm Hg. Il cristallise dans l'éthanol en aiguilles jaune pâle et on en recueille 1.53 g (40% de la théorie) fondant à 94°. Calculé pour $C_7H_3O_2N_2Cl$: C, 46.30%; H, 1.82%; N, 15.50%. Trouvé: C, 46.20%; H, 1.65%; N, 15.40%. Lorsque 0.70 g de 2-nitro-5-chlorobenzonitrile est bouilli à reflux pendant 24 heures avec 3.0 g de cyanure de potassium dans 20 ml d'éthanol à 50%, il se dégage de l'ammoniac, mais il ne se forme pas d'acide *m*-chlorobenzoïque. Des produits acides (0.346 g) seule une petite quantité (0.086 g)

d'une substance de p.f. 320° est obtenue par sublimation. Celle-ci n'est pas la lactone de l'acide 5-chloro-2-[5-chloro-3-oxy-indazyl-(2)]-benzoïque.

Après avoir bouilli à reflux pendant 24 heures 5.0 g d'acide 5-chloroanthranilique (5) avec 15.0 g de cyanure de potassium dans 50 ml d'éthanol à 50%, 3.0 g (60%) d'acide 5-chloroanthranilique peuvent être récupérés, mais il ne se trouve pas d'acide *m*-chlorobenzoïque.

REMERCIEMENTS

Nous remercions le Conseil national de Recherches du Canada, les firmes C.I.L. et Shell Oil, ainsi que l'Office de Recherches scientifiques de la Province de Québec, pour des bourses d'études accordées à l'un de nous (E.C.).

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FRIEDEL–CRAFTS REARRANGEMENTS IN BRANCHED CONDENSED RING SYSTEMS

I. OCTAMETHYLOCTAHYDROANTHRACENE[1]

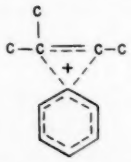
L. R. C. Barclay, A. H. Gray, and C. E. Milligan

ABSTRACT

Treatment of 1,1,4,4,5,5,8,8-octamethyl-1,2,3,4,5,6,7,8-octahydroanthracene ($C_{22}H_{34}$, I) with aluminum chloride produced a new hydrocarbon ($C_{22}H_{32}$, II) containing a conjugated olefinic double bond. Hydrocarbon II was proved to be 1,1,5,5,8,8-hexamethyl-3-isopropyl-5,6,7,8-tetrahydrobenzindene by spectral data, by oxidative studies, and by a synthesis of its reduction product, 1,1,5,5,8,8-hexamethyl-3-isopropyl-5,6,7,8-tetrahydrobenzindane (III). A benzenonium ion mechanism is postulated to explain the 1,2-phenyl shift accompanied by dehydrogenation in the formation of II from I. The detection of hydrogen in the off gas of the rearrangement supports this mechanism. A similar benzenonium ion mechanism can be applied to elucidate the mechanism of isomerization of tertiary to secondary alkylbenzenes reported in the literature.

INTRODUCTION

The branched condensed hydrocarbon octamethyloctahydroanthracene (I) provides an interesting system for conducting isomerizations under Friedel–Crafts conditions. Since in I the tertiary alkyl groups are part of a ring system, the nature of the products of rearrangement is expected to provide information on the mechanism of isomerization of tertiary to secondary alkylbenzenes. Such isomerizations were observed by Schmerling and West (1), who made the general observation that the formation of a tertiary alkylbenzene in the presence of catalysts such as aluminum chloride was really the exception rather than the general rule even when the alkyl halide used was tertiary. In the case of alkylation of benzene with *t*-pentyl chloride, they proposed that the tertiary alkylate is formed first and this is subsequently isomerized to the secondary alkylate by migration of a methyl or of a phenyl group. Schmerling and co-workers (2) later suggested that the rearrangement could take place through the cyclic bridged benzenonium ion—*



Roberts and Han (3) proposed the same mechanism to explain the conversion of *t*-pentylbenzene into 2-methyl-3-phenylbutane. Essentially this mechanism requires that the phenyl group is the migrating species in this arrangement rather than methyl migration. In a recent communication, however, Slaugh and Raley (4) made the general statement that Lewis acids produce no 1,2-phenyl migrations but rather lead to methyl migration processes.

In a system such as octamethyloctahydroanthracene (I) where the tertiary alkyl groups are in a ring system, a rearrangement where the phenyl group migrates through a benzenonium ion mechanism would lead to ring contraction. On the other hand if methyl groups migrate there would be no change in ring size. For this reason I was

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Contribution from the Department of Chemistry, Mount Allison University, Sackville, New Brunswick. Reported in part at the 43rd Annual Conference of the Chemical Institute of Canada, Ottawa, Ontario, June 14, 1960.

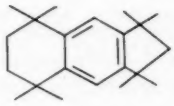
**The term "benzenonium ion" introduced by W. von E. Doering. Tetrahedron, 4, 178 (1958) is used on the recommendation of the referee.*

selected for some initial experiments on isomerization of tertiary alkylbenzenes under Friedel–Crafts conditions.

DISCUSSION OF RESULTS

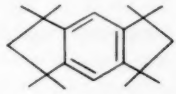
Treatment of octamethyloctahydroanthracene ($C_{22}H_{34}$, I) with aluminum chloride in tetrachloroethane or carbon disulphide converted it into a new crystalline compound, $C_{22}H_{32}$, II. The ultraviolet spectrum of II indicated the presence of a substituted conjugated olefinic double bond. There was a broad band at 260 mμ, ϵ = 11,220 and weaker bands at 288 mμ, ϵ = 2884 and 299 mμ, ϵ = 3162. The infrared spectrum of II showed a strong band at 11.3 microns attributed to 1,2,4,5-tetrasubstitution since this band was also observed for I. High-temperature mass spectral analysis of II established the parent mass to be 296, compared to 298 for I. There was also a strong peak in the mass spectrum of II at mass 253 corresponding to the loss of a C_3H_7 fragment. On catalytic reduction, II was converted into a compound III, $C_{22}H_{34}$, isomeric with I. This reduction product also lost a propyl fragment on high-temperature mass spectral analysis.

An important lead to the structure of III was provided by its ultraviolet spectrum. This spectrum was very similar to that of 1,1,3,3,5,5,8,8-octamethyl-5,6,7,8-tetrahydrobenzindane (IV) prepared by alkylating 1,1,3,3-tetramethylindane with 2,5-dichloro-2,5-dimethylhexane.



(IV)

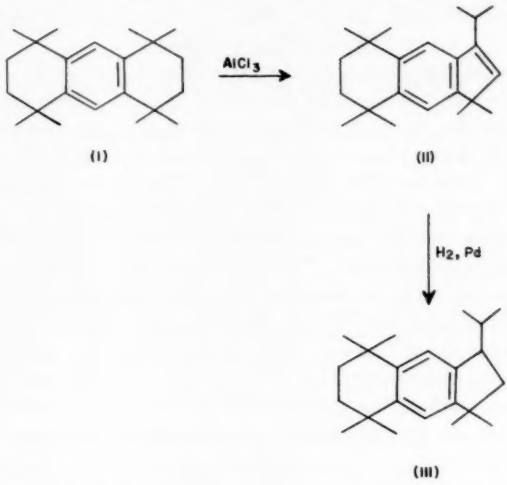
Hydrocarbon IV showed bands at 279 mμ, ϵ = 2408; 273.5 mμ (side band), ϵ = 1815; 270 mμ, ϵ = 2007; and a shoulder at 265.5 mμ. Hydrocarbon III showed bands at 280.5 mμ, ϵ = 2371; 275 mμ (side band), ϵ = 1908; 271.5 mμ, ϵ = 2067; and a shoulder at 267 mμ. The curves for III and IV had the same shape, the only significant difference was a shift in the spectrum of III of 1.5 mμ to longer wavelengths. On the other hand the spectrum of III showed distinct differences from that of octamethyloctahydroanthracene (I). The latter showed only two bands, at 278 mμ, ϵ = 1096, and 270 mμ, ϵ = 955. Furthermore the ultraviolet spectrum of I was practically identical with that of some other methylated octahydroanthracenes which we have synthesized such as the hexamethyl- and heptamethyl-octahydroanthracenes. The spectra of I and IV are both somewhat different from the spectrum of 1,1,3,3,5,5,7,7-octamethylhydrindacene (V) (5) —



(V)

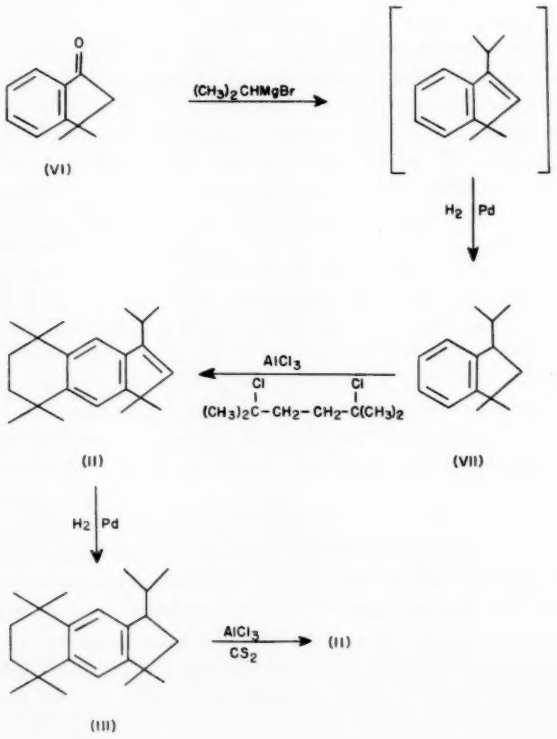
The latter had bands at 281 mμ, ϵ = 4725; 276 mμ, ϵ = 4243; 271.5 mμ, ϵ = 3760; and 267 mμ, ϵ = 2700. This shows that the degree of substitution around the non-aromatic rings has little effect on the character of ultraviolet absorption of the condensed ring systems. On the other hand the size of the non-aromatic rings has a more pronounced effect on the intensity and shape of the curves. Thus ultraviolet analysis provides a convenient means of deciding whether these ring systems are 6,6,6-, 6,6,5-, or 5,6,5-tricyclic systems.

The structures shown below for II and III seemed reasonable from the spectral evidence.



(I) (II) (III)

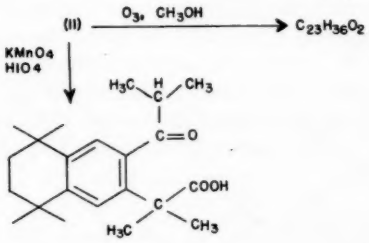
Compound II was tentatively assigned the endocyclic formulation since the exocyclic form would not be expected to lose a C_3H_7 fragment on mass spectral analysis. The structure suggested for III was confirmed by a classical synthesis which is outlined below—



(VI) (II) (VII) (III)

Friedel–Crafts alkylation of 3,3-dimethyl-1-isopropylindane (VII) with 2,5-dimethyl-2,5-dichlorohexane actually yielded the conjugated olefin II instead of the expected reduction product (III). This synthetic product was reduced for further identification and the reduction product proved to be identical with III.

The above synthesis confirmed the structure suggested for III but the position of the olefinic double bond in II remained to be established. The endocyclic formulation is in agreement with the work of Myhre (6), who produced a compound identical with our II by treatment of I with aluminum chloride. Although Myhre did not arrive at the structure of II, he hydroxylated it with permanganate followed by lead tetraacetate cleavage to produce a single product whose infrared spectrum indicated two carbonyl groups, an unconjugated aldehyde and a conjugated ketone. Our attempts to convert II into this dicarbonyl compound by ozonolysis in methanol yielded instead a mixture. By chromatography and recrystallization there was isolated from this mixture a compound of melting point 114–115° which had an ultraviolet spectrum practically identical with that of I. The infrared spectrum of this compound showed no carbonyl absorption but rather had two strong bands in the region of ether absorption at 8.85 and 9.45 microns. The compound analyzed for a methoxyl group and the ultimate analysis corresponded to $C_{23}H_{36}O_2$. The structure of this ozonolysis product was not definitely established. The spectral and ultimate analyses indicate a six-membered cyclic ether containing in addition a methoxyl group. Such a compound could only have formed from an endocyclic olefin, II.



The endocyclic formulation for II was confirmed in a more regular manner by permanganate–periodate oxidation. This oxidation yielded an aldehydic compound and an acidic compound both of which showed two strong carbonyl bands in the infrared at 5.90 and 5.75 microns. The acid had a strong band in the ultraviolet at 253 mμ attributed to the conjugated ketone. Its neutralization equivalent corresponded to the theoretical value for $C_{21}H_{31}OCOOH$. The conclusion arrived at by these degradative studies was later confirmed by the nuclear magnetic resonance spectrum* of II. This spectrum had a peak at −348 c.p.s. removed from tetramethylsilane, the internal standard. This peak was attributed to an olefinic proton which confirms the endocyclic formula II since the alternative exocyclic olefin could not have a hydrogen on the olefinic double bond.

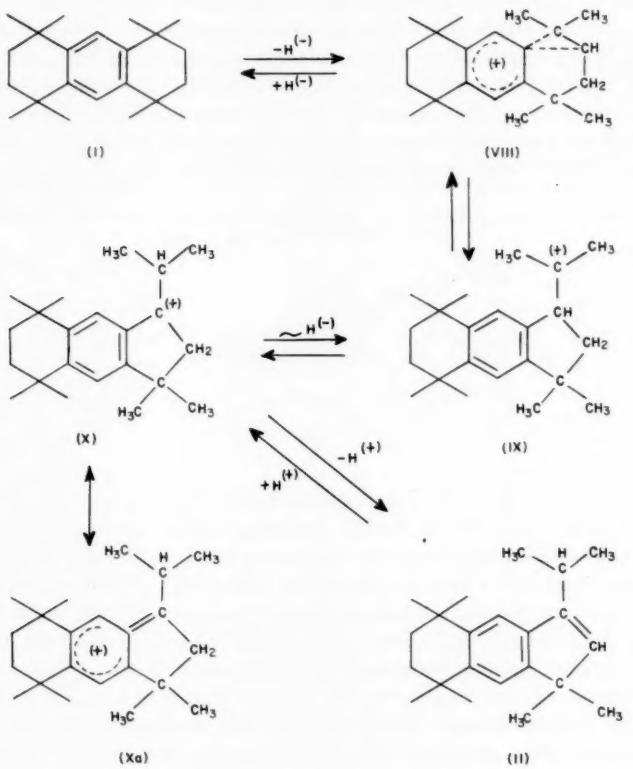
It is apparent that the more substituted exocyclic olefin is not favored in this reaction. A molecular model of the exocyclic olefin was made using Stuart and Briegleb models. In this model the methyl groups on the olefinic double bond are coplanar with the benzene ring resulting in a very strong steric interaction between one methyl and an ortho hydrogen. There is, of course, no such unfavorable interaction in the endocyclic compound II, which is therefore the principal product.

*We are indebted to Dr. Robert R. Fraser of the Chemistry Department, University of Ottawa, who measured and interpreted this spectrum.

Treatment of I with aluminum chloride in benzene did not yield the rearrangement compound (II). In this case the main product was 1,1,4,4-tetramethyltetralin. Thus, in benzene solution, the main reaction is disproportionation of I instead of rearrangement.

THE MECHANISM OF THE REARRANGEMENT

In a preliminary communication (7) it was suggested that the rearrangement of I to II proceeded via a hydrogen-bridged π-complex involving opening of a ring by displacement of a side chain with a proton. A more attractive mechanism for this 1,2-phenyl migration is a benzenonium ion mechanism. In this mechanism it is proposed that the catalyst extracts a hydride ion from a $-CH_2-$ group of a side chain to initiate the reaction. The benzene ring could participate in the displacement of the hydride ion by anchimeric assistance through a cyclic bridged benzenonium ion (VIII). The mechanism is outlined below:



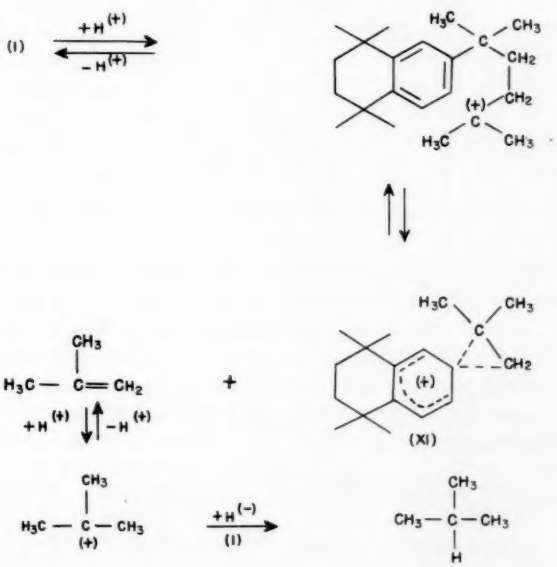
The carbonium ion X would be more stable than IX because the former is stabilized by resonance interaction with the directly attached benzene ring (X*a*). Loss of a proton from X produces the product isolated (II). It is not necessary for the reduction product III to be an intermediate in this reaction. We were unable to detect any of III by chromatographic fractionation of the reaction product. Of course this does not rule out the possibility of III being an intermediate especially since we found that aluminum chloride

treatment of III in carbon disulphide produced II. Treatment of III with aluminum chloride in tetrachloroethane alone did not yield sufficient II for characterization. The product in this case was a complex mixture containing some unchanged III, some non-crystalline products with strong absorption in the 260 mμ region, and a new crystalline compound with a strong band at 241 mμ and bands at 291 and 302 mμ. Such a spectrum is typical of extended conjugation. This material was not available in sufficient amount for a characterization but this spectrum indicates that it may have been formed by a rearrangement–dehydrogenation of both of the non-aromatic rings. Treatment of III with aluminum chloride and *t*-butyl chloride as a promoter in tetrachloroethane yielded II accompanied by the evolution of isobutane.

Nenitzescu (8) proposed that aluminum chloride exerts its strong catalytic action by formation of a strong acid $H^+AlCl_3\bar{O}H$ with traces of water. This strong acid initiates rearrangements by extraction of a hydride ion as follows:

$$R{-}H + H^+AlCl_3\bar{O}H \rightarrow R^+AlCl_3\bar{O}H + H_2.$$

The reaction can then be propagated as a chain reaction through carbonium ions which act as hydride ion acceptors. To support this concept they found traces of molecular hydrogen in the off gases from isomerizations. In this case the hydrogen was detected by combustion to water. Despite this discovery, Deno and co-workers (9) made the general observation that the hydride ion transfer reaction has the characteristic of ***not*** reacting with labile protons of the medium to form molecular hydrogen. It therefore was desirable to attempt to confirm the findings of Nenitzescu and co-workers by analyzing the off gases from our reaction directly for hydrogen. Vapor phase chromatographic and mass spectral analyses definitely showed the presence of hydrogen in the off gases. The major fraction of the off gases consisted of the hydrocarbons, isobutane and isopentane. Isobutane could have originated from I by side reactions as outlined below:



Elimination of isobutylene takes place by displacement of a side chain by the catalyst followed by fragmentation to yield isobutylene and the intermediate XI. The isobutylene could then be protonated by the catalyst to form a *t*-butyl cation which also would act as a hydride ion acceptor in promoting rearrangement of I. The production of isobutane thus takes place by a process which is just the reverse of the reaction proposed recently (5) to explain the cyclialkylation of 1,3,5-tri-*t*-butylbenzene through a benzenonium ion intermediate analogous to XI yielding I. When a trace of D_2O was added to the reaction during rearrangement of I, the infrared spectrum of the evolved isobutane showed a band in the C—D region at 4.6 microns. Deuterated isobutane would be expected to form if the isobutane originated as postulated. The isopentane could have originated by a process similar to that suggested for isobutane except that rearrangement must have taken place in a displaced side chain before the C_5 fragment was split off. No products were isolated from the rearrangement corresponding to the aromatic fragment XI. This intermediate probably undergoes polymerization to account for the resinous by-product formed in the reaction.

In order to substantiate the proposed mechanism for the conversion of I to II, attempts are being made to isolate the benzenonium ion intermediate as a stable salt.

EXPERIMENTAL

Apparatus and Procedures

The melting points are uncorrected. Ultraviolet spectra were recorded on a Beckman DK-2 ratio recording spectrophotometer using spectro-grade cyclohexane as solvent. Infrared spectra were recorded on a Perkin–Elmer Model 136 Infracord. Mass spectroscopic analyses were determined in an independent laboratory. A high-temperature inlet mass spectrometer was used for solids. The aluminum chloride was Fisher Certified Reagent, anhydrous sublimed, used as received. The rearrangement reactions were carried out at room temperature in an atmosphere of pure nitrogen. The apparatus was attached to a Perkin–Elmer Model 154-D vapor fractometer for direct analysis of the off gases. The product from the aluminum chloride – solvent mixture was worked up in the usual way and then in each case subjected to chromatography from petroleum ether on Fisher chromatographic alumina. The progress of the fractionation was followed by periodic analysis of the eluate from the column on the recording ultraviolet spectrophotometer. In this way the various possible components of the hydrocarbon mixture such as compounds I, II, and III could quite easily be detected and separated.

The Action of Aluminum Chloride on Octamethyloctahydroanthracene (I)

(A) In Tetrachloroethane

Octamethyloctahydroanthracene (10) (m.p. 220°) (5.00 g, 0.017 mole) was dissolved in 100 ml of purified tetrachloroethane and aluminum chloride (7.50 g, 0.056 mole) was added. The reaction was continued with stirring for 24 hours. Gas chromatographic analysis of the off gases showed that isobutane was slowly evolved throughout the course of the reaction. When a trace of water was added to the reaction, hydrogen gas was also detected on the vapor fractometer. Mass spectroscopic analysis of a sample of the off gases gave the following results:

nitrogen + air	98.5%,	*n*-pentane	0.1,
isobutane	0.7,	C_5 olefinic	0.1,
isopentane	0.5,	hydrogen	0.1.

Chromatograph fractionation of the crystalline residue (4.80 g) recovered from the reaction yielded 3.0 g, 60% of compound II from fractions 1 to 3. Fractions 4–8 (0.75 g) apparently consisted of a mixture of compounds. Recrystallization of fraction 4 (0.56 g) from ethanol followed by sublimation yielded colorless crystals, m.p. 96–97°.

Anal. Calcd. for $C_{22}H_{32}$: C, 89.12; H, 10.88. Found:* C, 89.07, 89.29; H, 10.99, 11.00.

The ultraviolet spectrum of this compound shows a broad band at 261 mμ, $\epsilon = 21{,}727$ and a broad band at 298 mμ, $\epsilon = 6215$. The infrared spectrum of this compound was clearly distinguishable from that of II. They both had a strong band at 11.3 microns attributed to 1,2,4,5-tetrasubstitution but there were differences in the 8–10 micron region and a strong band in II at 12.1 microns was absent in the lower melting compound. This band is most likely due to an out-of-plane =C—H deformation of the olefinic proton in II and its absence in the compound of melting point 96–97° indicates that the latter is the exocyclic isomer of II since this isomer would have no olefinic proton. A sample of this compound was dissolved in methanol and reduced with hydrogen at 4 atm over a palladium – calcium carbonate catalyst. This reduction product proved identical with III (below) by mixed melting point and ultraviolet spectrum. The remainder of the original reaction product was strongly adsorbed on the alumina column. It was removed by elution with acetone to yield 1.0 g of resinous material.

The crystalline material from chromatograph fractions 1 to 3 was recrystallized from ethanol to yield colorless plates, m.p. 133–134°.

Anal. Calcd. for $C_{22}H_{32}$: C, 89.12; H, 10.88. Found: C, 89.15; H, 10.51.

A 0.21-g sample of pure II was dissolved in methanol and reduced with hydrogen at 4 atm over 0.10 g of palladium – calcium carbonate catalyst to give a quantitative yield of product, m.p. 98–99°.

Anal. Calcd. for $C_{22}H_{34}$: C, 88.51; H, 11.49. Found: C, 88.35, 88.85; H, 11.37, 11.26.

This reduction product (III) showed a parent mass of 298 in the mass spectrum. There was also a strong peak at mass 255 corresponding to the loss of a C_3H_7 fragment. The infrared spectrum of III in carbon disulphide lacked the 12.1 micron band which was attributed to the olefinic proton in the infrared spectrum of II.

Another aluminum chloride reaction was carried out on I in tetrachloroethane as described above. In this case, 5 ml of water was added slowly to the reaction mixture and a deep blue-green solution resulted. This solution had an absorption band in the visible at 640 mμ. On standing, a solid separated from the tetrachloroethane solution. This solid was removed by centrifugation and washed twice with tetrachloroethane and three times with carbon tetrachloride. The solvents were removed by centrifugation to leave a blue crystalline powder. This material could be stored for several hours in a vacuum desiccator but it decomposed to a brown amorphous material on exposure to air. The infrared spectrum on a Nujol mull of this material showed strong hydroxyl absorption in the region of 3 microns. There was also a strong band in the unsaturation region at 6.1 microns and a band at 8.3 microns.

(B) In Carbon Disulphide

A rearrangement of I (5.0 g) was carried out in carbon disulphide under essentially the same conditions as described in section (*A*). Isobutane and hydrogen were detected in the off gases. On working up as in section (*A*), there was obtained 30% of the rearrangement product II, 60% of unreacted I and the remainder was resinous material. When the carbon disulphide solution was refluxed, the yield of II was at least 50%.

Analyses by Geller Laboratories, Bardonia, New York.

(C) In Benzene

Aluminum chloride (1.0 g) was added to a solution of I (2.0 g) in 50 ml of benzene and the mixture was stirred overnight. On working up the benzene layer, there was obtained 1.4 g of a clear oil. This oil was proved to be tetramethyltetralin by comparison of its ultraviolet spectrum and gas chromatographic analysis with synthetic tetramethyltetralin.

Synthesis of 1,1,5,5,8,8-Hexamethyl-3-isopropyl-5,6,7,8-tetrahydrobenzindane (III)

(A) 3,3-Dimethyl-1-isopropylindane (VII)

To the Grignard reagent, prepared from 6.76 g of isopropyl bromide (0.055 mole) and 1.36 g of magnesium (0.056 mole) in 25 ml of anhydrous ether, was added over 1 hour at 5° a solution of 8.5 g of 3,3-dimethyl-1-indanone (11) in 25 ml of dry benzene. The reaction mixture was refluxed for 2 hours with continuous stirring and worked up in the usual manner to yield 6.7 g (68.5%) of 3,3-dimethyl-1-isopropylindene, b.p. 80–84°/1.5 mm, $N_D^{28} = 1.5295$. This oil was reduced in methanol over a palladium catalyst with hydrogen at 2 atm yielding 6.5 g (98%) of 3,3-dimethyl-1-isopropylindane (VII). Distillation of this product yielded a colorless oil, b.p. 78–80°/2.5 mm. The ultraviolet spectrum of VII showed bands at 272 mμ, $\epsilon = 1175$ and at 265 mμ, $\epsilon = 933$ and was typical of similar indanes.

(B) Alkylation of VII with 2,5-Dimethyl-2,5-dichlorohexane. Characterization of III

To a solution of 1 g of VII (0.0053 mole) and 0.98 g of the dichloride (0.0054 mole) in 25 ml of carbon disulphide, was added 0.70 g of aluminum chloride (0.0053 mole) over a period of ½ hour with stirring which was continued for 3 hours. The product was worked up and chromatographed on alumina from petroleum ether to yield 1.3 g (80%) of white plates of melting point 125°. The ultraviolet and infrared spectra of this compound were identical with those of the rearrangement product II of octamethyloctahydroanthracene.

The alkylation product was reduced (in methanol solution) with hydrogen over palladium catalyst yielding 1.2 g (94%) of colorless needles. Purification was carried out by recrystallization from ethanol followed by sublimation yielding colorless needles, m.p. 100–101°. This compound was proved to be identical with the reduction product of II by mixed melting point and ultraviolet and infrared spectra.

Synthesis of 1,1,3,3,5,5,8,8-Octamethyl-5,6,7,8-tetrahydrobenzindane (IV)

Tetramethylindane (12) (5.00 g, 0.028 mole) and 2,5-dichloro-2,5-dimethylhexane (5.70 g, 0.031 mole) were dissolved in 10 ml of carbon disulphide and the mixture was cooled in an ice–salt bath. Anhydrous aluminum chloride (0.25 g, 0.002 mole) was added with stirring and the mixture allowed to warm to room temperature (2½ hours). The product was worked up and purified by recrystallization from ethanol to yield colorless needles (5.9 g, 74%) m.p. 195–198°; λ_{max} 279, $\epsilon = 2408$; 274.5 (side band), $\epsilon = 1815$; 270, $\epsilon = 2007$; and a shoulder at 265.5 mμ.

The Action of Aluminum Chloride on III

(A) In Carbon Disulphide

A 0.60-g sample of III was dissolved in 100 ml of carbon disulphide and reacted with 1.0 g of aluminum chloride under similar conditions as described for the reaction of aluminum chloride on I. Chromatographic fractionation of the reaction product yielded 45% of II.

(B) In Tetrachloroethane. The Effect of t-Butyl Chloride

A 1.0-g sample of III was dissolved in 100 ml of tetrachloroethane and treated with aluminum chloride as before. Chromatography of the product yielded 20% of III in the first fractions and a new compound (0.17 g, m.p. 177°) in later fractions. This compound had an intense band in the ultraviolet at 241.5 mμ and bands at 291 and 302 mμ. None of the hydrocarbon II was detected in the product.

Another aluminum chloride treatment of III was carried out under similar conditions except that, in this case, an equimolar amount of *t*-butyl chloride was added with the hydrocarbon. The reaction was allowed to continue for 8 hours during which time isobutane gas was detected in the off gases. Chromatographic fractionation of the reaction mixture from this run yielded 61% of the hydrocarbon II. None of the starting hydrocarbon (III) could be detected in the reaction mixture.

Oxidative Studies on II

(A) Ozonolysis

A 0.55-g sample of II was dissolved in 100 ml of absolute methanol. This solution was cooled to −25° and ozone (3%) was passed in slowly until a slight excess of ozone was detected. The ozonide was decomposed by shaking with hydrogen over a palladium–calcium carbonate catalyst. Distillation of the solvent left a non-crystalline residue. This was dissolved in petroleum ether and chromatographed on alumina. Elution with petroleum ether containing methanol removed a crystalline compound (0.1 g) m.p. 114–115°; λ_{max} 278, ϵ = 1222; 270 mμ, ϵ = 1056. The infrared spectrum of this compound in carbon tetrachloride showed no carbonyl absorption but had strong bands at 8.85 and 9.45 microns in the region of ether absorption.

Anal. Calcd. for $C_{23}H_{36}O_2$: C, 80.18; H, 10.05; O, 9.77; OCH_3, 9.01. Found: C, 80.15, 80.04; H, 10.40, 10.22; O, 9.72, 9.50; OCH_3, 11.60, 11.89.

(B) Permanganate–Periodate Oxidation

The hydrocarbon (1.40 g, 0.0047 mole) was dissolved in 200 ml of pyridine and oxidized with permanganate–periodate according to the method of Lemieux (13). The reaction mixture was worked up to yield 0.70 g (45%) of viscous neutral material and 0.50 g (31%) of crystalline acid. Recrystallization of the latter from petroleum ether yielded colorless crystals, m.p. 210°; λ_{max} 253 mμ, ϵ = 10,434. The infrared spectrum showed two strong bands in the carbonyl region, at 5.90 and 5.75 microns.

Anal. Calcd. for $C_{22}H_{32}O_3$: Neut. equiv. 344. Found: Neut. equiv. 344.

N.M.R. Spectrum of II

The N.M.R. spectrum was run on an 11% solution of II dissolved in carbon tetrachloride containing 1% of tetramethylsilane as internal standard. A peak appeared at −348 c.p.s. removed from tetramethylsilane and this peak was assigned to an olefinic proton.

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THE HYDROLYSIS OF A SERIES OF STRAIGHT-CHAIN ALKYL METHANESULPHONIC ESTERS IN WATER[1]

P. W. C. BARNARD[2] AND R. E. ROBERTSON

ABSTRACT

Rate data for the hydrolysis of methyl, ethyl, *n*-propyl, *n*-butyl methanesulphonate have been determined over sufficient range of temperature to permit an evaluation of the corresponding enthalpy, entropy, and heat capacity terms for the activation process. Changes in these derived parameters are related to characteristic differences in solvation and mechanism as a consequence of changes in the structure of the hydrolyzing ester.

Our knowledge concerning the details of hydrolysis of simple alkyl esters of strong acids in water have been extended recently by a study of isotope effects arising from changing the medium from H_2O to D_2O (1, 2, 3) and from various secondary deuterium isotope effects (4, 5, 6). In principle, further information should be made available from a consideration of the changes in the derived parameters, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, $\Delta C_p^{\ddagger}$ but the theoretical basis for the interpretation of changes in these parameters suffers from such uncertainty that to an important degree, relating changes in these parameters with changes in structure amounts to no more than confirming changes anticipated from other evidence of mechanism. The greatest uncertainty would appear to lie in $\Delta H^{\ddagger}$ and $\Delta C_p^{\ddagger}$, differences in $\Delta S^{\ddagger}$ being somewhat easier to interpret. Our purpose in this paper, therefore, was to determine the rate data for hydrolysis of a series of alkyl methanesulphonates over sufficient range of temperature that reliable values of the enthalpy, entropy, and heat capacity of activation could be determined, and to show how changes in these parameters are consistent with the solvation of sulphonates and with changes to be expected in mechanism from lengthening the carbon chain.

EXPERIMENTAL METHODS AND MATERIALS

The methanesulphonic esters used in this study were synthesized by conventional methods (7, 8). The physical constants are given in Table I. The method used in determining rates of hydrolysis, in temperature measurement and control were identical in all respects with those used in determining kinetic data for the benzenesulphonates (9)

TABLE I

Physical properties of the methanesulphonic esters

Alkyl group	n_D^{25}	% purity*	d_4^{24}
Methyl†	1.4138	99.8	1.30056
Ethyl	1.4151	100.3	1.20492
n-Propyl	1.4210	99.1	1.11483
n-Butyl	1.4255	99.6	1.10853
n-Amyl	1.4298	101.6	1.08242
n-Octyl	1.4378	97.1	1.01521

*Based on the neutral equivalent % purity

$$= \text{neutral equivalent} \left[\frac{\text{calculated}}{\text{observed}}\right] \times 100.$$

†B.p. 2mm. 55–55.5° C.

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with the obvious change that sodium methanesulphonate (0.003 *M*) was used as the backing electrolyte. The conductance cells were the ones used in our study of the benzenesulphonates and initially good agreement between parallel runs in different cells or successive runs in the same cells was not possible. These discrepancies disappeared, however, following repeated washings with the backing electrolyte, interspersed with several hours "aging" at 100° C in the presence of a reaction solution. Similar treatment was found to be necessary for "new" cells, but here the aging process required fewer "dummy" runs to satisfy what was assumed to be the absorptive capacity of the walls. When such equilibrium was established, reproducibility of the rate appears to be independent of the cell within the stated limits shown in the tables.

The temperature was controlled to ±0.01° C or better and was determined with a platinum thermometer and a Mueller bridge (L. and N. 8069).

First-order rates were calculated by the Guggenheim method as described in our earlier paper (9).

RESULTS AND DISCUSSION

The rate data for a series of temperatures together with the average deviation of n repetitive runs at the same temperature are given for the methyl, ethyl, *n*-propyl, and *n*-butyl esters in Table II. It was found that the temperature dependence of the rates

TABLE II

Kinetic data for the hydrolysis of a series of methanesulphonic esters

Temp., °C	$k_1 \times 10^5$, sec^{-1}	n
(*a*) Methyl methanesulphonate		
0.00_0	$0.159_6 \pm 0.0009$	3
5.00_0	$0.333_1 \pm 0.0022$	4
9.95_0	$0.691_2 \pm 0.0034$	4
14.99_8	$1.38_2 \pm 0.001$	3
19.99_4	$2.69_5 \pm 0.002$	3
24.90_8	$5.00_4 \pm 0.015$	4
29.99_5	$9.33_0 \pm 0.031$	3
34.99_9	$16.7_0 \pm 0.05$	4
39.85_2	$28.7_9 \pm 0.14$	4
44.78_6	$49.2_4 \pm 0.28$	4
49.93_1	$84.0_2 \pm 0.12$	2
49.92_3	$83.9_5 \pm 0.06$	2
59.70_4	$217._5 \pm 0.2$	3
$\log_{10} k = 7125.354/T - 17.9380 \log T + 62.9900$		
(*b*) Ethyl methanesulphonate		
9.81_7	$0.497_8 \pm 0.0008$	3
19.85_2	$2.01_1 \pm 0.006$	4
29.41_0	$6.80_8 \pm 0.006$	3
39.83_9	$23.6_5 \pm 0.29$	3
50.04_9	$71.6_3 \pm 0.08$	3
60.03_4	$197._4 \pm 0.11$	4
70.00_3	$501._2 \pm 0.5$	7
79.76_9	$116_9 \pm 3.0$	3
$\log_{10} k = 7204.552/T - 17.4479 \log T + 61.9329$		
(*c*) *n*-Propyl methanesulphonate		
89.98_9	182.8 ± 0.6	4
89.97_8	182.6	1
84.97_5	123.2 ± 0.1	2
79.99_6	$82.2_8 \pm 0.05$	2
79.98_7	$82.1_7 \pm 0.18$	4
74.13_4	$49.9_1 \pm 0.2$	4
70.00_0	$34.6_8 \pm 0.02$	4
64.99_5	$22.0_3 \pm 0.01$	4
60.00_0	$13.8_3 \pm 0.05$	4
54.99_8	$8.51_4 \pm 0.01$	4
49.99_8	$5.16_4 \pm 0.03$	3
44.96_4	$3.05_4 \pm 0.016$	4
40.30_9	$1.83_8 \pm 0.001$	3
29.98_4	$0.560_3 \pm 0.003$	3
20.16_2	$0.164_7 \pm 0.0004$	4
$\log_{10} k = -6498.02712/T - 13.1105373 \log T + 48.719322_5$		
(*d*) *n*-Butyl methanesulphonate		
89.91_7	186.3 ± 0.5	3
84.99_0	127.6 ± 0.2	3
79.97_8	85.38 ± 0.08	4
74.98_4	56.32 ± 0.05	3
69.94_1	36.38 ± 0.04	3
65.05_8	23.55 ± 0.0	2
59.98_4	14.80 ± 0.03	3
49.89_5	$5.54_8 \pm 0.009$	4
44.75_3	$3.25_2 \pm 0.003$	4
40.00_0	$1.96_4 \pm 0.001$	4
$\log_{10} k = -6163.0693/T - 11.319_4 \log T + 43.2238$		
(*e*) *n*-Amyl methanesulphonate		
84.973	124.1 ± 0.2	2
84.967	124.0 ± 0.1	2
74.97_1	54.26 ± 0.1	3
64.95_1	$22.6_0 \pm 0.05$	3
(*f*) *n*-Octyl methanesulphonate		
65.00_2	23.68 ± 0.1	2
74.95_4	$58.1_7 \pm 0.1$	2
85.06_2	131.7 ± 0.5	2

in every case could be expressed within the accuracy of reproducibility of the rate determination by an empirical equation of the form

$$\log k = A/T + B \log T + C \quad [1]$$

and the equations immediately under each section, Table II, give the corresponding constants for each ester as determined by the method of least squares. If we accept the usual transition-state hypothesis for the case where $d\Delta H^*/dT$ is non-zero, but $d\Delta C_p^*/dT$ is invariant with temperature, then the constant of equation [1] may be interpreted as follows: $A = -(\Delta H_0^*/2.303\ R)$; $B = (\Delta C_p^*/R-1)$; $C = \{(\Delta S_0^* - \Delta C_p^*)/2.303\ R + \log_{10} k/h\}$. Thermodynamic parameters characterizing the hydrolysis of the four esters, calculated according to the above assumptions are given in Table III. No claim is made here that

TABLE III

Thermodynamic parameters for the hydrolysis of a series of methanesulphonates for 50.0° C

Ester	H^*, cal/mole	S^*, cal/mole deg	C_p^*, cal/mole deg
Methyl	20,441	−14.08	37.6
Ethyl	21,120	−12.31	36.7
n-Propyl	20,672	−16.43	28.0
n-Butyl	20,289	−15.37	24.5
n-Amyl	20,440	−15.1	—
n-Octyl	20,100	−15.9	—

the assumption that $d\Delta C_p/dT = 0$ is not in some measure arbitrary; and it may well be that when data over a wider range and with greater precision are available, ΔC_p^* will be found to vary with temperature. The present data do not suggest, however, that $d\Delta C_p/dT > 0.1$ cal/deg mole. Estimated values of ΔH^* and ΔS^* values for *n*-amyl and *n*-octyl methanesulphonate from limited rate data (Table II) are included in Table III but these terms have much larger probable errors than those determined for the preceding compounds.

In the hydrolysis of the alkyl methanesulphonates there seems no basis to doubt that bond fission occurs at the C—O bond just as in the hydrolysis of the alkyl benzenesulphonates (10, 11). This conclusion is supported by product analysis and neutral equivalent determinations which also indicate that the reaction goes to virtual completion under the experimental conditions. The possibility that elimination would become a competing reaction path in this series of straight-chain alkyl methanesulphonates is discounted by the small proportion of olefine found (Table IV) and it is by no means

TABLE IV

Olefine production in the hydrolysis of a series of methanesulphonic esters in water

Ester	Temp., °C	% olefine*
Ethyl	60	0.52±0.05†
n-Propyl	100	1.26±0.03
n-Butyl	60	1.60±0.16

*As determined by the method of Byrne and Johnstone (13).
†Reproducibility from parallel determinations.

certain that the olefine so formed represents a competing path and is not formed subsequently to the transition state.

In current terminology, the hydrolysis of the methyl methanesulphonate in water occurs by an "intermediate" mechanism, i.e., an S_N2 mechanism in which the solvent provides the nucleophile and in which solvation of the forming anion is assumed to be a significant driving force. Evidence from relative rates of hydrolysis with and without the presence of OH^- (k_{OH^-}/k_{H_2O}) (12) and the relative deuterium isotope effect derived by replacing the methyl hydrogens by deuterium (k_H/k_D) (4, 5) support the contention that in hydrolysis, nucleophilic interaction between oxygen of one particular water molecule and the methyl carbon is less in hydrolysis for the methyl methanesulphonate than for the methyl halides in the transition state, but is not absent. Both methyl halides and sulphonates show an inverse α-deuterium isotope effect on hydrolysis which can be rationalized in terms of interference with the C—H out-of-plane bending frequency by the partially bonded water molecule on the side opposite to the leaving group (Table V).

TABLE V

Deuterium isotope effects for the hydrolysis of the methanesulphonates

Ester	αd_2	βd_2	γd_3	Ref.
Methyl*	0.95	—	—	4
Ethyl	1.037	1.027	—	6
n-Propyl	1.036	1.074	0.94	6

*αd_3

Deuterium substitution of ethyl and *n*-propyl esters in the β-position leads to k_H/k_D values greater than unity. The effect is small and it would be difficult, on the basis of these isotope effects alone, to distinguish between the possibility that the observed effect arises from some weak interaction between the β-H and the partially empty *p*-orbital developing at the rear of α-C or is the consequence of a reduction in non-bonded interactions or arises from other causes. The empirical observation that deuterium substitution on the γ-carbon gives an inverse isotope effect ($k_H/k_D > 1$) analogous to the effect of α-substitution is an indication that the activation process requires a configuration which reduces the freedom of γ-C—H vibration. In a recent paper Leffek, Llewellyn, and Robertson discuss these problems in greater detail (6). Here we shall examine the very much larger indications of mechanistic changes with chain lengthening apparent in the derived parameters, ΔH^*, ΔC_p^*, and ΔS^*, particularly the latter.

Entropy of Activation

The relation of structure to the derived values of ΔS^* for hydrolysis will be considered in this section with reference to two specific examples (1) a comparison of ΔS^* values for the hydrolysis of MeBr and MeMes and (2) the changes in ΔS^* with chain lengthening within the methanesulphonate series.

Example I

The difference in the rate of hydrolysis of methyl bromide and methanesulphonate ($k_{MeBr}/k_{MeMes} = 7.6$) is much less than would be expected from differences in ΔH^* or ΔS^* alone (Table VI), a circumstance frequently observed (14, 15, 16, 17, 18) and usually associated with solvation differences either in the initial or transition states or both. It is known, of course, from differences in k_{OH^-}/k_{H_2O} ratios (12) that the hydrolysis of methyl bromide requires a greater degree of nucleophilic interaction than methyl methanesulphonate but this could hardly contribute as much as 1–2 e.u. to $\delta_{RX}\Delta S^*$. Hence some 5–6 e.u. must be associated with $\delta_{RX}\Delta S^*$ solvent.

TABLE VI

A comparison of kinetic parameters for the hydrolysis of MeBr and MeMes

	$k_1 \times 10^{-5}$, sec^{-1}	$\Delta H^{\ddagger}$, cal/mole	$\Delta C_p^{\ddagger}$, cal/mole deg	$\Delta S^{\ddagger}$, cal/mole deg	Ref.
MeBr	1.11	24,142	46.5	−2.91	14
MeMes	8.44	20,441	37.6	−10.83	This work

Following the argument of Robertson, Heppolette, and Scott (17) the charge development on Br^- at the transition state will be about 0.8 e. Hence applying Laidler's hypothesis (19) that $\Delta S_0^0 \alpha z^2$, the entropy change to be associated with the quasi-ionic Br^- will be about $(0.8)^2 \times 12 = -8$ e.u. where the entropy of solvation for Br^- ion is −12 e.u. for a standard state of 1 mole/l. in both phases (20). The corresponding parameter for the methanesulphonate ion is not known but may be estimated from Altschuler's empirical equation (21) for oxy anions. Assuming the same charge development for the methanesulphonate as for the bromide the corresponding entropy change will be −14.3 e.u.

If the above assumptions are correct, there is here a difference of about 6 e.u. in the solvation of the quasi-ionic anions in the transition state and this will account for the major observed differences in $\Delta S^{\ddagger}$. To infer that the initial states are comparably solvated, however, would be incorrect.

In aqueous solutions it is now accepted that a non-electrolyte may be described as being surrounded by a solvation shell in which water–water interaction is greater than the interaction in bulk water or of water–solute interaction in solution (22, 23, 24). The formation of this initial-state solvation shell is characterized by a negative component in the entropy which appears to bear some inverse relationship to the polarity of the solute. Thus the entropy of solution for the gas solution equilibrium for MeBr and methane are both about −18 e.u. (17), indicating that in substituting —Br for —H in methane, the increased size of the substituent, which would imply a more negative shift in entropy of solvation, is cancelled by the increased polarity of the substituent.

Obviously the fraction of this value which must be associated with increased water–water interaction about the Br atom is difficult to judge, but it would seem that a value of 5–6 e.u. implied by the difference

$\Delta S^{\ddagger}_{\text{solvent}}$ (transition state for Br^-)	−8 e.u.
$\Delta S^{\ddagger}$	−2.91
	−5.09

would not be unreasonable. Evidence both from the solvent isotope effect (3) and particularly from the temperature dependence of the solvent isotope effect (25) suggests that the water molecules adjacent to the sulphonic group are already interacting with the sulphonic oxygens in the initial state with a corresponding loss in rotational entropy. The same inference may be drawn from the enhanced solubility in water which the sulphonic groups introduce into organic molecules. Taking the calculated entropy loss associated with the quasi-ionic sulphonic transition state (−14.3 e.u.) and subtracting the observed value of $\Delta S^{\ddagger}$, we may estimate that this initial-state loss corresponds to about 3–4 e.u. Hence, summing up, the entropy difference observed in the hydrolysis of the two esters probably arises largely in the transition state. The differences in the initial state are smaller but the physical characteristics of the initial-state solvation are quite different.

We have noted above that $(S^0_{solv})^{gas}_{soln}$ for MeBr and methane are both about -18 e.u. but so far have neglected to consider the contribution to ΔS^* from reorganization about the Me group. The initial-state solvation shell has a large negative component due to increased water–water interaction. Granted that the entropy assignments to the anionic moiety are correct, any change in entropy about the methyl group will have to come out of the respective residuals (-5.09 and -3, or -4). For simplicity we have assumed such differences to be small for the methyl esters.

Example II

In hydrolysis, the structural change Me → Et may be assumed to lead to a more ionic transition state and an increase in steric hindrance to nucleophilic interaction. This conclusion based largely on relative rates in solvolysis and the effect of added bases on such rates (12) has gained further support from the results for secondary deuterium isotope effects (6). In the present series the difference in rates of hydrolysis between the methyl and ethyl esters ($k_{Et}/k_{Me} = 0.85$) is much smaller than normal for S_N2 displacements and tends to belie larger changes in the detailed mechanism suggested by differences in ΔH^* and ΔS^* (Table III).

A more ionic transition state for the ethyl ester would seem to require a more negative ΔS^* and this is probably true for that component of $\delta_R\Delta S^*$ associated with the quasi-anion even though the net $\delta_R\Delta S^*$ for the structural change Me → Et is 1.7 e.u. positive. Of the sources of positive entropy which could contribute to the positive residual in $\delta_R\Delta S^*$ that due to the diminished nucleophilic interaction is probably small. A more likely source is associated with the breakdown of a larger initial-state solvation shell but it is not clear how to estimate this contribution.

The introduction of a γ-methyl group to Et— (to give *n*-propyl) need not produce added steric hindrance to nucleophilic interaction (26) and would not be expected to have a large direct electronic effect on the seat of reaction; nor would the change in reactivity ($k_{n\text{-Pro}}/k_{Et} = 0.72$) lead us to anticipate the observed shift in $\Delta S^*(\delta_R\Delta S^* = -4.12$ e.u.). Such a change in entropy appearing suddenly in a straight-chain series is not unusual and has been attributed to loss of rotational freedom in the transition state (6, 27) due to either increased crowding or to solvent exclusion. The latter is the hypothesis adopted by Evans and Hamann (28) and by Everett, Landsman, and Pinsent (29) to account for the gradual negative shift in entropy with chain lengthening in the ionization of a series of straight-chain acids and amines. While "solvent exclusion" may be a factor here, the contrast between the gradual shift in entropy for ionization of the amines and acids and the abrupt shift at *n*-propyl and also the results of secondary deuterium isotope studies are evidence of some other larger contributing factor. Leffek, Llewellyn, and Robertson (6) showed that whereas the β-H deuterium isotope effect is greater than unity, the γ-substitution led to a value of $k_H/k_D < 0.95$ for four different displaced groups —a result consistent with increased crowding in the transition state. It is suggested that this alteration in spacial relationships is the direct consequence of rehybridization of α-C in the activation process. The normal secondary deuterium isotope effect for β-H is small and may either arise from the same cause or be taken as possible evidence of some degree of weak interaction between the β-H and the partially empty *p*-orbital but is of the wrong sign were solvent exclusion the source of loss of rotational freedom.

The constancy of ΔS^* for the hydrolysis of the longer straight-chain alkyl mesalates suggests that the above discussion for *n*-propyl may be applied to the higher members of the series and further that solvation changes are not influenced by chain length beyond the second or third member of the series.

Heat Capacity of Activation

The temperature dependence of $\Delta H^{\ddagger}$ is assumed to be linear in T. Although in some measure arbitrary the range of temperature covered by the investigation and the accuracy of the rate determinations would not justify a more-refined treatment.

The actual values of the temperature coefficients of $\Delta H^{\ddagger}$ for the hydrolysis of the methanesulphonic esters are of the same magnitude and sign as for the benzenesulphonates and less negative than for the halides (17). The major factor determining the latter difference would appear to be the same: the temperature dependence for the "stability" of the initial-state solvation shell or that part thereof which must be broken down in the activation process. The change in $\Delta C_p^{\ddagger}$ with the change Me → Et is negligible, but there is a significant reduction in the negative value of $\Delta C_p^{\ddagger}$ for the structural change Et → *n*-Pro.

Such a change is in qualitative agreement with the shift to be expected where there is a decrease in rotational freedom for a simple model of a harmonic oscillator (31), the entropy becoming more negative and the $\Delta C_p^{\ddagger}$ more positive. The stiffening here, however, arises from a different cause than that suggested by Kirkwood and adopted by Evans and Hamann (26) and by Everett, Landsman, and Pinsent (27) since in the work described by the latter authors chain stiffening was assumed to arise as a consequence of the exclusion of the low polar hydrocarbon from the charge center by the solvent. Here the loss of rotational freedom appears to arise at least in part as an incidental to the decrease in $\Delta H^{\ddagger}$ as a consequence of the β-hydrogen interaction with the forming empty p-orbital coupled with a possible change in the non-bonded interaction between the terminal methyl and the leaving group.

The Enthalpy of Activation

The $\Delta H^{\ddagger}$ values reported in Table III are similar to the corresponding values for the benzenesulphonates and some 4–5 kcal lower than for the halides. The latter difference may be attributed to solvation differences in the initial state, in particular, to the evidence of strong solute–water interaction in the initial state for the sulphonates compared to the enhanced water–water interaction about the halide. Granted this explanation for the difference, we are left with the uncomfortable question of why the residuals are so similar.

The change in $\Delta H^{\ddagger}$ with increasing length of the alkyl group, while small, follows the same pattern as for the benzenesulphonates, with an increase from Me → Et where the α-methyl increased the steric hindrance to nucleophilic interaction without supplying through electron release or hydrogen interaction a driving force sufficient to compensate for this loss. The further lengthening of the chain (Et → *n*-Pro) leads to increased β-hydrogen interaction, loosening of the β-C—H bond, and a lowering of $\Delta H^{\ddagger}$ which partially compensates the negative shift in $\Delta S^{\ddagger}$ attributed to loss of rotational freedom. The influence of the specific nature of the leaving group is apparent here; $\delta_R \Delta H^{\ddagger}$ having values (17) (in kcal) for I^- of 0.1, Br^- −0.98, methanesulphonate −0.4, and benzenesulphonate −0.56.

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CONSTITUTION OF A GLUCOMANNAN FROM TAMARACK (LARIX LARICINA)[1]

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ABSTRACT

A hemicellulose fraction containing D-mannose, D-glucose, and D-galactose in a ratio of 70:25:3 has been isolated from tamarack wood. The product was homogeneous under conditions of free boundary electrophoresis and of sedimentation in the ultracentrifuge. Hydrolysis of the fully methylated hemicellulose yielded 2,3,4,6-tetra-*O*-methyl-D-glucose (1.2%); 2,3,4,6-tetra-*O*-methyl-D-galactose (2.2%); 2,3,6-tri-*O*-methyl-D-glucose (24.0%); 2,3,6-tri-*O*-methyl-D-mannose (68.8%); 2,3-di-*O*-methyl-D-mannose (1.6%); and 2,3-di-*O*-methyl-D-glucose (1.7%). This data and that from periodate oxidation indicated that the glucomannan had a linear backbone of approximately 35 (1 → 4) linked β-D-glucopyranose and β-D-mannopyranose units; approximately two thirds of the chains were terminated at the non-reducing ends by D-galactose and the remainder by D-glucose. Branching, if present, must occur through C_6 of the hexoses in the main chain.

Investigations of glucomannans from various gymnosperms have shown a similar basic structure (1–5). They consist of D-glucose and D-mannose units (ratio 1:3–4) joined by β-1,4-glucosidic bonds into linear chains. Two additional structural features about which there are divided opinions concern the presence of branching in the molecule, and the presence and structural attachment of D-galactose units associated with glucomannans. Much of the evidence for branching has been based on the presence of the dimethyl sugars found during methylation studies. It is well known that such evidence may be of questionable significance and the general consensus of opinion at the present time is that most glucomannans are unbranched (2, 6, 7, 8). Galactose units, when present, occur predominantly as non-reducing end groups (2, 7, 8, 9).

The present investigation of the glucomannan of tamarack was undertaken as part of a systematic study of the polysaccharides of this species. It was desirable also to compare the composition and structure of the glucomannan from tamarack with those from other coniferous species.

Extraction of tamarack holocellulose with 17.5% sodium hydroxide yielded a crude hemicellulose fraction which on acid hydrolysis gave D-mannose, D-glucose, D-galactose, D-xylose, L-arabinose, and a uronic acid component. The acidic xylan was precipitated as its "Cetavlon" (cetyl trimethyl ammonium hydroxide) complex. From the soluble residue, the glucomannan was recovered by gradient addition of ethanol. The yield of glucomannan was approximately 20% of the crude hemicellulose, a relatively large proportion having coprecipitated with the xylan–"Cetavlon" complex. Acid hydrolysis of the glucomannan and chromatographic examination of the sugars showed galactose, glucose, and mannose with only traces of xylose and arabinose. Quantitative estimations showed that galactose, glucose, and mannose occurred in the hemicellulose in a ratio of 3:25:70. The hemicellulose behaved as a single compound on examination in the ultracentrifuge and in moving boundary electrophoresis.

The methyl ethers obtained from methanolysis of the fully methylated glucomannan were analyzed by gas–liquid partition chromatography (10, 16). This method provided not only a means of identification of the methylated sugar glycosides but also yielded

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quantitative data as to the relative amounts of methylated sugars. The free methylated sugars were separated by paper chromatography using the appropriate solvents and the results are shown in Table I. The main methylated sugars were found to be 2,3,6-tri-*O*-methyl-D-mannose and 2,3,6-tri-*O*-methyl-D-glucose which showed that the glucose and mannose residues were joined by 1,4 glycosidic bonds in the original hemicellulose. The linkage was presumably of the β type because of the negative specific rotations both of the original and the methylated hemicellulose; these values were increased on hydrolysis. The 2,3,4,6-tetra-*O*-methyl-D-galactose was the only methylated galactose found and therefore the galactose units must have occurred exclusively as non-reducing end groups. Although less than the required amount of galactose was recovered as 2,3,4,6-tetra-*O*-methyl-D-galactose, no evidence for any other methylated galactose was found. A small amount of glucose occurred as non-reducing end groups as shown by the presence of 2,3,4,6-tetra-*O*-methyl-D-glucose. Apparently mannose did not constitute any end groups as no tetramethyl mannose was detected. Approximately two thirds of the glucomannan chains were terminated by D-galactose and the remainder by D-glucose. One tetramethyl sugar residue was present for every 32 hexose residues. This value is of the same general order as the 34 hexose residues per reducing end group as found by hypoiodite oxidation and the value of 40 as determined by gas–liquid chromatography of the methylated sugars.

Periodate oxidation of the hemicellulose showed that 1.10 moles of periodate per mole of anhydrohexose sugar was consumed. Formic acid production was 0.11 mole per anhydro sugar unit and indicated a chain length of 33 hexose units. The absence of any glucose or mannose in the hydrolyzate of the product obtained by borohydride reduction of the periodate-oxidized hemicellulose showed that all monosaccharide units had been oxidized and there was no branching through C_2 or C_3 of these units. If any branching occurred it would have to be through C_6. The erythritol and glycerol produced in the degradation reactions must have come from $1 \rightarrow 4$ linked sugar units and non-reducing terminal residues respectively.

At variance with the prediction of a straight-chain structure is the finding of dimethyl sugars which may be interpreted as indicating branch points in the molecule. If the amounts of dimethyl sugars found on hydrolysis had their origin from branch points in the hemicellulose, then the amount of recovered tetramethyl sugars which represents terminal groups becomes insufficient. Even allowing for less than a quantitative yield of tetramethyl galactose, there would still be a shortage of end groups. The conclusion that the amount of end groups found is substantially correct is supported by the fact that estimation of the degree of polymerization using these values is in good agreement with that found by periodate oxidation, by gas–liquid chromatography, and also by reducing end group estimation. It seems likely then that the dimethyl sugars do not represent branch points in the molecule but are products of demethylation or incomplete methylation.

It is apparent that D-galactose is an integral part of the glucomannan molecule. If it were to occur as a separate entity, then methylated galactoses other than tetra-*O*-methyl-D-galactose should be found on hydrolysis. So far, these have not been found even by the sensitive gas–liquid chromatographic method. Terminal galactose units could originate from an admixture of galactoglucan or (and) galactomannan with the present polysaccharide. While the presence of such polysaccharides is not excluded no positive evidence for them has been found.

It is apparent that the tamarack glucomannan is similar to most glucomannans of coniferous origin. The glucose-to-mannose ratio, specific rotation, and general structural features correspond clearly to those of other glucomannans (2, 4, 11, 12). While species

differences may well account for variations in composition and structure of the glucomannans, the methods of preparation may also contribute to the differences. For example, a glucomannan prepared from Sitka spruce by Dutton and Hunt (7) had a glucose-to-mannose ratio of 1:9; using another method of preparation Aspinall *et al.* (6) obtained a glucomannan from the same species having a glucose-to-mannose ratio of 1:2.5.

Evidence for branching through C_2 and C_3 in the glucomannans of western hemlock (13), Norwegian spruce (14), and Scots pine (12) have been provided through examination by the Smith degradation procedure (15). Examination of the glucomannan of jack pine (2) yielded neither D-glucose nor D-mannose after periodate oxidation, a result which is in agreement with that reported above for tamarack.

Further differences between the glucomannan of tamarack and those of some other species are the sugars constituting the non-reducing terminal group. Western hemlock (13) and Scots pine (12) have non-reducing terminal units of both D-glucose and D-mannose while Norwegian spruce (14), Sitka spruce (6), and loblolly pine (9) have non-reducing terminal units of D-mannose but none of D-glucose. Some of these differences may have been caused by the difficulty in separating the 2,3,4,6-tetra-*O*-methyl ethers of D-glucose and D-mannose (6) a difficulty which is obviated by the use of gas–liquid partition chromatography (16).

The occurrence of D-galactose in glucomannans has been noted by several investigators and it has not always been found to be a part of the glucomannan molecule. A polysaccharide from loblolly pine (17) having a composition similar to that of tamarack was considered to be a mixture of galactomannan and glucomannan. Further investigation (9) of the same polysaccharide showed that the chains of 27–33 sugar units were terminated by non-reducing units of D-galactose and D-mannose. The methyl ethers of D-galactose obtained from the hydrolysis of methylated glucomannan from western red cedar were considered to have originated from a contaminating galactoglucomannan (8). D-Galactose was found in glucomannans isolated from Sitka spruce (7) and Scots pine (12) but in each instance further purification removed it. Glucomannans prepared from western hemlock (13), Norwegian spruce (14), Sitka spruce (6), and white spruce (4) were devoid of D-galactose.

Fragmentation analyses of the tamarack glucomannan are being undertaken in this laboratory to determine the structural relationships of the D-galactose units and the sequence of the hexose residues in the molecule.

EXPERIMENTAL

All specific rotations are equilibrium values unless otherwise stated, melting points are corrected, and all evaporations were done at 35° C or less.

Paper Chromatography

Chromatographic separations were carried out on filter paper using the following solvent systems (v/v):

(A) pyridine:ethyl acetate:water (2:1:2),
(B) methyl ethyl ketone:water:ammonia (100:50:3),
(C) ethanol:benzene:water:ammonia (47:200:14:1),
(D) *n*-butanol:ethanol:water (40:11:19),
(E) *n*-butanol:pyridine:water (5:4:5).

Separations were made by the descending method on either Whatman No. 1 or No. 3MM filter paper. Sugars were located on the paper by the *p*-anisidine spray reagent (18);

non-reducing sugar derivatives were detected by silver nitrate and sodium hydroxide sprays (19).

Preparation of the Hemicellulose

Starting material for the preparation was a crude hemicellulose obtained from tamarack (*Larix laricina* (Du Roi) Koch) chlorite holocellulose by extraction with sodium hydroxide solution (17.5%). Chromatographic examination of an acid hydrolyzate showed galactose, glucose, mannose, arabinose, xylose, and a uronic acid were present.

Crude hemicellulose (50 g) was added gradually to water (2.5 liters) and stirring was continued at 0° C for 3 days. Undissolved material (4.6 g) was removed by centrifuging and the supernatant was diluted to 4.5 l. with water. An aqueous solution of 2% "Cetavlon" (cetyl trimethyl ammonium hydroxide) (1 liter), hydroxide form was prepared from the bromide form by stirring with silver oxide (13 g) for 1/2 hour and then removing the silver salts by filtration. Addition of "Cetavlon" to the solution of the hemicellulose with stirring gave a sticky precipitate which settled out on standing overnight. The supernatant was removed by decantation and its pH adjusted to 5.0 by acetic acid. The first hemicellulose fraction (I) was precipitated by adding ethanol to a concentration of 24%, after its removal a second fraction (II) was precipitated by adding ethanol to 50% concentration. The precipitates were recovered by centrifuging, washed successively with 50% ethanol (3 times), 100% ethanol (3 times), and ethyl ether (3 times). Ether was removed on the steam bath and the hemicellulose was dried *in vacuo* at room temperature. The yields were: fraction I, 2.14 g, fraction II, 10.0 g. Chromatographic examination of hydrolyzates showed that fraction II contained galactose, glucose, and mannose, fraction I contained xylose in addition to galactose, glucose, and mannose. On the basis of these results, fraction II, which appeared to be a galactoglucomannan, was selected for subsequent investigations.

The polysaccharide was dissolved in dilute alkali to give a clear solution $[\alpha]_D^{25}$ −30° (*c*, 1% in 0.5 *N* sodium hydroxide). Hydrolysis of a sample (12 mg) in a sealed tube with *N* sulphuric acid for 12 hours and examination of the sugars by paper chromatography (solvents A and E) showed the presence of mannose, glucose, a small amount of galactose, and a trace of xylose. No uronic acids could be detected.

The ratio of the sugars in the hydrolyzate was determined using the method of Dubois *et al.* (20) and was found to be mannose:glucose:galactose, 70:25:4. A more accurate measurement of the amount of galactose present was provided by using gas–liquid chromatographic determination of the fully methylated sugars as described by Adams and Bishop (21). This latter method gave the previous ratio of mannose and glucose but the galactose content was 2.7%. Xylose was present in only trace amounts.

Examination of the hemicellulose in a 0.05 *M* borate buffer by moving boundary electrophoresis carried out in a Spinco model H Tiselius-type apparatus showed only a single sharp peak. Mobility measurements gave the value, $\mu = 6.71 \times 10^{-5}$ cm^2 volts^{-1} sec^{-1}. The same solution was centrifuged in a Spinco model E ultracentrifuge at 59,000 r.p.m. and showed only one symmetrical peak which is indicative of a single compound.

End Group Determination by Hypoiodite

A slightly modified Willstätter–Schudel method (22) was used for reducing end group determination of the hemicellulose. Samples in triplicate (50 mg each) were dissolved in 5 ml of *N* sodium hydroxide and then 2.5 ml of 0.02 *N* iodine was added. The solutions along with suitable controls were kept in stoppered flasks in the dark for 3 hours. After acidification with 10 ml of *N* sulphuric acid, the iodine was titrated with 0.01 *N* sodium thiosulphate. One reducing group was found to occur per 34 anhydrohexose units.

Periodate Oxidation

Duplicate samples of the hemicellulose (100 mg) were dissolved in water (50 ml) and oxidized by 0.1 *M* sodium metaperiodate (50 ml) in the dark at room temperature. Suitable reagent blanks were prepared under the same conditions. At the intervals shown in the table below, analyses were made for periodate consumption and formic acid production (23). The results given in moles per mole anhydrohexose unit were as follows.

Time, hours	26	77	130	179	221	300
Periodate consumption	0.84	0.98	1.07	1.10	1.15	1.18
Formic acid production	0.027	0.067	0.078	0.094	0.103	0.130

In a separate experiment, the hemicellulose was degraded according to Smith's procedure (15) as follows: hemicellulose (200 mg) was dissolved in water (100 ml) and oxidized with 0.1 *M* sodium metaperiodate (100 mg) for 240 hours at room temperature. Excess periodate was destroyed by the addition of ethylene glycol and the solution was dialyzed for 24 hours. The non-dialyzable material was concentrated to 25 ml and potassium borohydride (250 mg) was added. After 72 hours, the solution was neutralized with acetic acid and deionized by Amberlite IR-120 and IR-45. The resulting solution was evaporated *in vacuo* to dryness and the boric acid removed by repeated evaporation with methanol. The dried residue (65 mg) was dissolved in water (10 ml) and an aliquot (1 ml) was hydrolyzed with *N* hydrochloric acid for 6 hours at 100° C. Paper chromatography of the hydrolyzate in solvent D showed erythritol as the main component with glycerol present in small amounts. No monosaccharides were detected in the hydrolyzate.

Methylation of the Hemicellulose

Hemicellulose (5.0 g) was dissolved in 20% sodium hydroxide (50 ml) and methylated by the dropwise addition of dimethyl sulphate (50 ml) and 45% sodium hydroxide (100 ml). The methylation procedure was repeated four more times and the partially methylated product recovered by dialysis. Repetition of the methylation gave a product which was extracted by chloroform. Fractionation from chloroform solution by the addition of light petroleum (b.p. 30–60°) gave a methylated fraction (5.1 g) having a methoxyl content of 40.6%. Four further methylations were carried out using Purdie's reagents (methyl iodide (75 ml) and silver oxide (10 g)). The methylated hemicellulose (4.3 g) $[\alpha]_D^{25}$ −25.2° (*c*, 1% in chloroform) had a methoxyl content of 43.5% (theoretical for fully methylated hexosan 45.6%) and showed no hydroxyl absorption in the infrared.

Methanolysis and Hydrolysis of the Methylated Hemicellulose

A solution of the methylated hemicellulose (4.0 g) in 8% methanolic hydrogen chloride (60 ml) was refluxed on a boiling-water bath for 15 hours. A sample of the mixture of the methyl glycosides (5 mg) was removed for examination by gas–liquid partition chromatography (16).

The presence of the methyl glycosides of the following methyl sugars was indicated:

2,3,4,6-tetra-*O*-methyl-D-glucose,
2,3,4,6-tetra-*O*-methyl-D-galactose,
2,3,6-tri-*O*-methyl-D-glucose,
2,3,6-tri-*O*-methyl-D-mannose.

Smaller peaks which were not resolved were glycosides of dimethyl sugars.

The methanolysis mixture was freed of methanol and then hydrolyzed by heating it

with 0.5 *N* hydrochloric acid (25 ml) at 100° C for 22 hours. The acid was neutralized with silver carbonate and the methylated sugars were recovered as a clear syrup (4.1 g), $[\alpha]_D^{25}$ +11.3° (*c*, 1% in water). Chromatographic examination on filter paper (solvent B) indicated the same methyl sugars as found by gas–liquid chromatography, but in addition the dimethyl portion had been resolved into two components.

Separation of Methylated Sugars

The mixture of methylated sugars was separated on sheets of Whatman No. 3MM filter paper using solvent B. The sugars were eluted with water and the solutions were taken to dryness. The residues were extracted with methanol, clarified with charcoal, and the syrups were recovered and dried. Yields of methylated sugars along with their R_g values are given in Table I.

TABLE I

Methylated sugars from hydrolysis of methylated hemicellulose

Methylated sugars	R_g solvent B	Yield (mg)	%
2,3,4,6-Tetra-*O*-methyl-D-glucose	0.98	27	1.2
2,3,4,6-Tetra-*O*-methyl-D-galactose	0.81	50	2.2
2,3,6-Tri-*O*-methyl-D-glucose	0.66	557	24.1
2,3,6-Tri-*O*-methyl-D-mannose	0.55	1587	68.8
Dimethyl sugar 1	0.30	38	1.6
Dimethyl sugar 2	0.23	40	1.7

Identification of Methylated Sugars

2,3,4,6-Tetra-O-methyl-D-galactose

The syrup had the same R_g value (0.81) in solvent B as an authentic sample of 2,3,4,6-tetra-*O*-methyl-D-galactose. The sugar (24 mg) was dissolved in ethanol (1 ml), freshly distilled aniline (20 mg) was added, and the mixture was refluxed for 3 hours. Removal of the solvent in a desiccator yielded white needles which were recrystallized from ethanol to yield 2,3,4,6-tetra-*O*-methyl-*N*-phenyl-D-galactosylamine (17 mg), m.p. and mixed m.p. 196–197° C, $[\alpha]_D^{25}$ −138° (*c*, 0.9% in pyridine).

2,3,4,6-Tetra-O-methyl-D-glucose

This sugar had the same mobility on a paper chromatogram in solvent B and on paper electrophoresis in borate buffer as authentic 2,3,4,6-tetra-*O*-methyl-D-glucose.

The sugar (9 mg) was dissolved in ethanol, aniline (6 mg) was added, and the mixture was refluxed for 2 hours. The fine needles which formed on removal of the solvent had a melting point of 128–130° C. Two recrystallizations from ethyl ether – light petroleum yielded 2,3,4,6-tetra-*O*-methyl-*N*-phenyl-D-glucosylamine, m.p. 136–137°; reported value 137–138° (24).

2,3,6-Tri-O-methyl-D-glucose

The sugar separated on paper chromatograms was decolorized with charcoal. The solution was concentrated to a syrup, ethanol was added, and on slow evaporation a portion of the sugar crystallized. Recrystallization several times from ethanol – ethyl ether – light petroleum yielded 2,3,6-tri-*O*-methyl-D-glucose, m.p. 121° C, $[\alpha]_D^{24}$ +70.0° (*c*, 0.5% in water); reported values m.p. 121–123° C, $[\alpha]_D$ +70° (25).

Preparation of the 1,4-di-*p*-nitrobenzoate according to Rebers and Smith (32) yielded the crystalline derivative, m.p. 189–190° after recrystallization from methanol. Reported value m.p. 189–190° (26).

*2,3,6-Tri-O-methyl-*D*-mannose*

This sugar had the same mobility on a paper chromatogram (Solvent B) as an authentic sample of 2,3,6-tri-*O*-methyl-D-mannose. The aniline derivative was prepared as described above and yielded the crystalline 2,3,6-tri-*O*-methyl-*N*-phenyl-mannosylamine, which on repeated recrystallization from ethyl acetate – petroleum ether, had a melting point of 131–133° C (reported value 133° (28)). The 1,4-di-*p*-nitrobenzoate derivative was prepared as described above and after one recrystallization from methanol had a melting point of 187–188°; reported value 187–188° (26).

*2,3-Di-O-methyl-*D*-mannose*

Demethylation of a small amount of the syrup (5 mg) with boron trichloride (17) showed that mannose was the main product with minor amounts of glucose also present. On paper electrophoresis in borate buffer the main di-*O*-methyl mannose had an M_g value of 0.11. It was separated from other minor components on paper chromatograms using solvent C. The sugar (32 mg) was converted into the 1,4,6-tri-*p*-nitrobenzoate derivative using the same procedure described above. After several recrystallizations from methanol the melting point was 192°, reported value 194° (29).

*2,3-Di-O-methyl-*D*-glucose*

Glucose was the main product found on demethylation along with a minor amount of mannose. Paper chromatography (solvent C) separated the main component which on paper electrophoresis in borate had an M_g value of 0.12. The sugar which appeared to be 2,3-di-*O*-methyl-D-glucose could not be obtained in crystalline form. On refluxing it in ethanol solution with aniline, crystalline 2,3-di-*O*-methyl-*N*-phenyl-D-glucosylamine was obtained. Recrystallization from ethyl acetate gave a product having m.p. 132°; reported value 134° (30).

Other Dimethyl Sugars

Along with the two di-*O*-methyl sugars described above, two others, a di-*O*-methyl mannose (M_g 0.07) (solvent C) and a di-*O*-methyl glucose were recovered in trace amounts. They were tentatively identified as 2,4-di-*O*-methyl-D-mannose and 2,4-di-*O*-methyl-D-glucose on the basis of demethylation and paper electrophoretic and chromatographic evidence.

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CHALKOGENIDES OF THE TRANSITION ELEMENTS

III. MOLYBDENUM DITELLURIDE[1,2]

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ABSTRACT

$MoTe_2$ prepared by dry synthesis from the elements at 460° C and annealed at 600° C has a layer structure of the *C7* type with $a_0 = 3.5182 \pm 14$ Å and $c_0 = 13.9736 \pm 40$ Å. The parameter of the tellurium atom has been determined from closely reproducible X-ray diffractometer powder intensities as 0.621 ± 1. The nearest-neighbor co-ordination polyhedron of the molybdenum atom is a trigonal prism with a Mo—Te distance of 2.716 ± 12 Å. The distance of nearest approach of the tellurium atoms between layers is 3.945 ± 25 Å and thus greater than the similar distance between chains in metallic tellurium. It is shown that the observed intensities are not compatible with a stacking sequence of the *C27* type, which differs from the *C7* arrangement in the geometry of the co-ordination polyhedra of the metal atoms.

INTRODUCTION

It has been recently reported that molybdenum disulphide does not always have a crystal structure of the *C7* type, whose prototype it is, but that it can exist as at least two, and possibly three, polymorphs (1, 2, 3, 4). The two structures of the sulphide which are known in detail, i.e., the hexagonal *C7* structure and the rhombohedral form first described by Bell and Herfert (3) and later structurally reinterpreted by Jellinek *et al.* (4), are both layer structures consisting of planar sheets of superposable hexagonal networks of molybdenum and sulphur atoms stacked parallel to the basal plane. They differ in the sequence and period of displacement of the molybdenum and sulphur networks with respect to each other. The sequence is . . .AMABNBAMABNBAMA . . . for the *C7* form and . . . APACMCBNBAPACMCBNBAPA . . . for the rhombohedral form (A, B, C refer to sulphur layers, M, N, P, to molybdenum layers), but in both cases the stacking sequences result in trigonal-prismatic nearest-neighbor co-ordination of the molybdenum atom. Other sequences are theoretically possible, in some of which the environment of the metal atom is trigonal antiprismatic (distorted octahedral). A structure of this type would be, for example, the *C27*-type structure known from β-CdI_2, which Hägg and Schönberg (1) proposed as a possible MoS_2 structure to account for the observed X-ray intensities of some of their MoS_2 samples showing reportedly large disagreement between I_o and $I_c(C7)$.*

Although the crystal structure of the corresponding telluride, $MoTe_2$, has not been determined before, it was usually assumed that it belonged to the *C7* group; in reference 5, for instance, this follows by implication. When evidence for the polymorphism of MoS_2 appeared, it became clear that the telluride need not necessarily have the stacking arrangement of a *C7* compound and even if it does, the structure may be of lower symmetry, as has been found to be probably the case with the corresponding wolfram compound (6).

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[2]*Part II of this series appeared in Can. J. Chem.* **39**, *297 (1961).*
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**The relationship between the C7 and the rhombohedral form of MoS_2 is the same as that between the C27 and the C19 ($CdCl_2$) structure, except that the metal co-ordination is trigonal prismatic in the first pair and distorted octahedral in the second.*

As far as we know, the occurrence of the *C7* type of structure is restricted to chalkogenides of niobium (4), molybdenum, tantalum (7), wolfram, rhenium (8), and possibly hafnium.* These compounds and the rhombohedral polymorphs of the disulphides of molybdenum, niobium, and tantalum are, moreover, almost the only known instances of structures in which the metal atom has trigonal-prismatic nearest-neighbor co-ordination,† which would seem to indicate a strong preference for this rather than for octahedral co-ordination. The observed bulk diamagnetism of MoS_2 (11) (and also of WTe_2 (13)) is in agreement with the assumption that the trigonal-prismatic co-ordination is the result of d^4sp bonding. Further support of this contention comes from the appreciable diamagnetic anisotropy of single crystals of molybdenite, the negative susceptibility parallel to the hexagonal axis being almost twice as large as that in the direction normal to the axis (12). Such magnetic behavior with its strong temperature dependence and the appreciable electrical conductivity of molybdenite along the basal plane both point to the presence of a system of largely delocalized mobile π electrons within the MoS_2 layers; the existence of such a system can again be explained from the d^4sp orbital configuration on the molybdenum atom, or more particularly from its $\pi(p^2d)$ system of trigonal symmetry. The telluride, which, too, has been shown to be diamagnetic (13), can accordingly be expected to have a *C7* structure or its rhombohedral modification. Furthermore, unless Hägg and Schönberg's MoS_2 preparations were paramagnetic, an explanation of the observed discrepancies in the diffraction intensities of these samples cannot be advanced on the basis of a *C27*-type structure with its sp^3d^2 (or d^2sp^3) bonding and its associated magnetic moment.

On the other hand, ReS_2 (14) and WS_2 (15) have been reported to be paramagnetic. The effective magnetic moment of ReS_2 is small and independent of temperature, but natural WS_2, tungstenite, has been stated to be strongly paramagnetic with a curious temperature dependence and a pronounced anisotropy. The effective moment of tungstenite at room temperature was found higher than would correspond to the "spin-only" value for two unpaired 5*d*-electrons. The *ad hoc* explanation for the paramagnetism of tungstenite profered by Dutta and Chowdhury (15) and based on the assumption of a *C7* structure, fails to establish why molybdenite, for which the same qualitative arguments apply, is diamagnetic. If the reported magnetic behavior of tungstenite is genuine and not caused by ferromagnetic or strongly paramagnetic impurities in the natural material‡ the orbital configuration on the tungsten atom cannot be d^4sp. The paramagnetism could be due to d^3p^3 or d^3sp^2 bonding, but then the stereochemistry of the WS_6 group would not be consistent with the $\bar{6}$ symmetry of the regular trigonal prism. The difference in co-ordination could be brought to light by crystal-structure analysis, but a sufficiently accurate detailed study of WS_2 has not yet been made. If orbital configurations of geometries different from that of d^4sp are, however, admitted to explain the paramagnetism of WS_2, one should bear in mind that this last configuration is not the only one to account for the observed diamagnetism of $MoTe_2$, but that this telluride might conceivably exist with a d^4p^2 configuration on the molybdenum atom. Since neither the magnetic properties of WS_2 nor its crystal structure has been established beyond doubt

*This case is now under investigation in this laboratory.

†In the *B8 (nickel arsenide) structure the atoms with trigonal-prismatic co-ordination are the non-metal atoms. A similar situation obtains, for instance, in* Re_2B, Ru_2B_3, *and other borides (9), and also in some carbides and phosphides. In the borides* $RhB_{\sim 1.1}$ *and* PtB, *however, which have been reported to have anti-*NiAs *structures, the nearest-neighbor co-ordination of the metal atoms is trigonal prismatic (10).*

‡*The tungstenite used by Dutta and Chowdhury was, to the authors' own admission, impure, but chemical analyses of the mineral are not shown. The impurity content varied with the source of the material; the spread of the experimental densities of the individual crystals (method not stated) was very appreciable, 7.00–8.2.*

to either eliminate or include the possibility of co-ordination other than trigonal prismatic in the above group of dichalkogenides, prediction of the crystal structure of $MoTe_2$ is not entirely straightforward.

As for the differences caused by the stacking sequences of MX_2 layers of a particular type, either trigonal-prismatic or octahedral, polymorphs of this kind would not be expected to have widely dissimilar lattice energies. This is borne out by the relative readiness with which mixed sequences are formed in, for instance, cadmium or nickel bromides, although the ratio of the atomic radii does to some extent determine the stacking arrangement (cf. α-CdI_2 and $CdCl_2$).

In view of the contradicting statements in the literature concerning the molybdenum etc. dichalkogenides and since the tellurides of the above elements have so far received only scanty attention, we thought it of interest to investigate whether the trigonal-prismatic co-ordination of molybdenum, which is apparently characteristic for the typical molybdenum disulphide and diselenide, is preserved in the ditelluride; and if this is the case, whether the structure corresponds to the *C7* type, with or without distortion, or to another stacking arrangement.

EXPERIMENTAL

The ditelluride was prepared by dry synthesis from the elements *in vacuo* in much the same way as previously WTe_2 (6). Fansteel molybdenum powder type 352 of average particle size of 4–5 microns and of specified minimum purity of 99.9% and specified minimum impurity content of 0.015% C, 0.125% O, and 0.02% Ni, was reduced before use with purified hydrogen at 690–700° C. The tellurium metal was kindly donated by Canadian Copper Refiners, Ltd., and contained, according to the supplied analysis (in p.p.m.), 0.4 Cu, 3.0 Al, and 0.5 Mg. Hg (detection limit 2 p.p.m.), Pb (0.5), Fe (1), As (10), Sb (0.5), Sn (0.5), Bi (0.5), Ni (1), Cr (0.5), Zn (10), Ag (0.1), Na (4), and Si (1) were not detected.

A stoichiometric mixture of molybdenum and tellurium powders totalling 15 g was sealed in a degassed, evacuated tube of clear quartz and kept at 460° C for 16 hours. On removal from the furnace the tube was opened and the reacted mixture crushed lightly to pass a 125-mesh screen. The thoroughly mixed powder was then resealed and annealed at 600° C for 48 hours. The product was a loose dark-gray powder of uniform appearance consisting of very fine needles and platelets. The crystals were too small and often intimately intergrown to be suitable for a single-crystal study. No foreign particles were detected under magnifications up to 30 diameters.

Specimens for X-ray powder diffraction were prepared by mounting $MoTe_2$ powder that had been crushed to pass completely a 325-mesh screen, on very thin pyrex fibers coated thinly and uniformly with vacuum grease. Powder photographs were taken in 114.6-mm Straumanis-type cameras with filtered Cu K, Fe K, and Cr K radiations. Powder specimens for the Norelco diffractometer were prepared by sifting the annealed powder through a 325-mesh screen on a cylindrical aluminum specimen mount coated evenly with a thin, flat layer of stiff silicon grease. The diffractometer patterns were obtained with rotating specimens using 1/2, 1, and 4° slits and a pulse-height analyzer. They were used for the integrated intensities only. The same wavelengths were used as are quoted in the second paper of this series.

RESULTS

The films were of surprisingly good quality, considering the frequently poor definition of the diffraction lines obtained with tellurides of the transition elements. As could be

expected, the photographs taken with filtered Cu K radiation had the best appearance and were used in the final determination of lattice parameters. All lines could be indexed on a hexagonal unit cell (Table I). After six cycles of refining a and c by least squares

TABLE I

Observed and calculated $\sin^2\theta$ values and X-ray powder intensities for $MoTe_2$ (Cu $K\alpha$ radiation)

	$10^4 \cdot \sin^2\theta$					$10^4 \cdot \sin^2\theta$			
*hkl**	calcd.	obs.	I_c†‡§	I_o‡§	*hkl**	calcd.	obs.	I_c†‡§	I_o‡§
002	0122	0124	22.0	21.0	218	6429	6427	5.0	5.1
004	0487	0493	12.7	13.0	10.14	6605	6611	0.7	1.0
100	0640	0641	37.0	40.4	306	6858	6852	1.5	2.3
101	0670	0673	9.0	10.9	20.12	6944	—	0.4	—
102	0762	0764	3.7	3.3	219	6947		0.2	
103	0914	0918	100	100	10.15	7488	7494	1.3	2.1
006	1096	1109	3.4	3.8	21.10(1)	7512		0.0	
104	1127	1141	6.2	6.3	21.10(2)	7550	7533		
105	1401	1403	36.8	36.9	220	7682	7679	5.6	
106	1736	1753	2.4	2.8	20.13(1)	7690	7706	3.1	
110	1921	1922	27.3	41.8	308(1)	7696		11.1	
008	1948	1967	8.6		20.13(2)	7730	7739		
112	2043	2048	3.0	3.4	308(2)	7736			31.2‖
107	2132	2147	3.2	3.8	00.16(1)	7777	—	1.7	
114	2408	2414	7.6	7.7	222(1)	7791	7796	0.7	
200	2561	2568	4.3	5.1	222(2)	7829	7835		
108	2588	2608	7.6	8.8	11.14(1)	7871	7887	3.3	
201	2591		1.1		11.14(2)	7913	7928		
202	2683	—	0.3	0.4	21.11(1)	8150	8159	15.6	
203	2835	2843	14.4	15.2	224(1)	8155		2.4	19.3
116	3017		3.8		21.11(2)	8191	8202		
00.10	3044	3030	0.0	5.9	224(2)	8196			
204	3048		1.3		310(1)	8303	8307		
109	3106	—	0.2	—	310(2)	8350	8348	3.2	3.8
205	3322	3336	8.2	8.8	311(1)	8338		0.9	
206	3657	3676	0.7	0.8	10.16(1)	8416	8430	2.9	
10.10	3684		0.0		312(1)	8430		0.4	4.1
118	3869	3887	16.2	18.4	10.16(2)	8460	8480		
207	4053	4063	1.2	1.2	312(2)	8472			
10.11	4323	4351	8.9	11.5	20.14(1)	8510	8525	1.0	
00.12	4383	—	0.4		313(1)	8581	8581	14.6	14.9
210	4481		3.4		313(2)	8625	8625		
208	4509	4505	3.3	7.8	226(1)	8763	8766	2.3	
211	4511		1.0		30.10(1)	8790	8802	0.1	
212	4603	—	0.4	0.4	314(1)	8794		1.6	3.5¶
213	4755	4768	13.0	13.3	30.10(2)	8835	8856		
11.10	4965	4974	0.1		314(2)	8839			
214	4968		1.2	2.0	21.12(1)	8849		1.3	
10.12	5023	5042	0.5		315(1)	9068	9065	13.1	12.6
209	5027		0.1		315(2)	9114	9109		
215(1)	5234	5249	8.8	8.7	20.15(1)	9392	9404	2.5	
215(2)	5260	5267			316(1)	9402		1.6	
216	5577	5592	0.8	1.0	10.17(1)	9420		0.0	4.0¶
20.10	5605		0.0		20.15(2)	9441	9451		
300	5762	5760	5.3		316(2)	9449			
10.13(1)	5773	5789	2.9	8.8	10.17(2)	9468			
10.13(2)	5803	5815			21.13(1)	9608	9613	15.0	
302	5884	—	0.6	0.7	228(1)	9613		27.3	37.0
00.14	5966	5971	0.5	2.6	21.13(2)	9657	9659		
217	5973		1.5		228(2)	9662			
20.11(1)	6232	6247	6.4		11.16(1)	9694	9706	28.7	29.8**
304(1)	6238		2.1		11.16(2)	9745	9754		
20.11(2)	6264			11.3	317(1)	9797	9797		
304(2)	6270	6281			317(2)	9846	9844	6.1	
11.12	6304		1.7		00.18(1)	9843		0.0	

*Resolved α-doublets are indicated by (1) and (2). †For $z = 0.621$; temperature factor not included. ‡Normalized to $I(103)$. §Intensities of the α_1 and α_2 components are taken together. ‖Overlap. ¶Extent of maxima uncertain. **Diffractometer cutoff.

using Nelson–Riley extrapolation for reflections with $\theta > 30°$ the final values of the lattice parameters were $a_0 = 3.5182 \pm 14$ Å, $c_0 = 13.9736 \pm 40$ Å, and $c_0/a_0 = 3.972$. The volume of the unit cell is 149.79 ± 17 Å^3.

The density of $MoTe_2$ (125−) was determined in the same way as described in Part II of this series. Average of three determinations gave $d_4^{25} = 7.681 \pm 18$ g/cm^3, which corresponds to 1.974 $MoTe_2$ per unit cell. This density compares rather more favorably with the density calculated from the lattice parameters, 7.784 ± 9 g/cm^3, than the value quoted by Morette (13), $d_4^{15} = 7.60 \pm 1$ g/cm^3, and is only -1.28% lower than the X-ray density. It is difficult to say whether the discrepancy has a real significance as regards the existence of molybdenum and tellurium vacancies in the structure.* Unreacted molybdenum and tellurium in amounts lower than the minimum amounts capable of producing observable diffraction lines cannot be detected in a stoichiometric $MoTe_2$ sample by density measurement because of the almost identical densities of $MoTe_2$ and a 1:2 mixture of molybdenum and tellurium.

Reflections of the (hkl) type with $h-k = 3n$, $l = 2n+1$ were absent. This condition is satisfied in eight space groups, viz., D_{6h}^4—$P\,6_3/mmc$, D_{3h}^4—$P\,\bar{6}2c$, C_{6v}^4—$P\,6_3mc$, D_6^6—$P\,6_322$, C_{6h}^2—$P\,6_3/m$, C_6^6—$P\,6_3$, D_{3d}^2—$P\,\bar{3}1c$, and C_{3v}^4—$P\,3/c$, but the symmetries and equipoints of these space groups are compatible not only with the *C7*, but also with, for instance, the *C27* structure, which has been claimed as possible for some MoS_2 samples (cf. Introduction).

The first model tried was a *C7* structure (space group D_{6h}^4—$P\,6_3/mmc$) with 2 Mo in $2(c)$: $\pm(1/3, 2/3, 1/4)$ and 4 Te in $4(f)$: $\pm(1/3, 2/3, z)$; $\pm(1/3, 2/3, 1/2-z)$, $z_{Te} = 0.625$ $(= 5/8)$. A set of intensities was calculated for Cu $K\alpha$ radiation using Thomas–Fermi atomic scattering factors tabulated in reference 18. The agreement between I_o and I_c was good, but it was felt that the integrated powder intensities, which had been obtained by careful planimetering of several diffractometer charts, would justify further refinement. Six other values of z varying from 0.618 to 0.628 were then tried. Since out of the 70 observable reflections with $I_c \geqslant 0.5$ (normalized to $I_o(103)$) only 26 were fully resolved, the extent of agreement could not be assessed from the reliability index, $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, customary in structure analysis from single-crystal data. However, the sum $\sum |I_o - I_c|$, though not an unambiguous measure of the progress of refinement, was found to be quite sensitive to variations in z. The agreement of I_o and I_c for $z = 0.621 \pm 1$, which was the value corresponding to the minimum of the difference sum located analytically for a parabolic least-squares fit, was indeed remarkably good (Table I). The *C7* structure adopted in the first trial can thus be considered correct, the existence of homometric structures compatible with the observed dimensions and symmetry of the unit cell being not very probable.

The close agreement of the intensities also demonstrates that the diffractometer specimens were free from orientation effects which are frequently present in specimens of compounds with fully developed layer structures. Stacking disorder in our $MoTe_2$ preparation must have been negligible for the same reason. The increase of $|I_c - I_o|$ with θ for individual reflections was so small that it did not justify inclusion of an isotropic temperature factor. In particular, there was no systematic weakening of I_o for reflections with $h-k \neq 3n$ with increasing l, nor was there selective line-broadening affecting particular orders.

As for the possibility that $MoTe_2$ has a *C27*-type structure (space group $C_{6v}^4 - P\,6_3mc$),

**Similar, and even greater, differences between pycnometric and X-ray densities have been reported for wolfram disulphide (16, 17).*

it is readily seen that a model structure with 2 Mo in 2(*b*): $\pm(1/3, 2/3, 1/4)$, 2 Te in 2(*b*): $(1/3, 2/3, z)$, $(2/3, 1/3, 1/2+z)$, 2 Te in 2(*a*): $(0, 0, -z)$, $(0, 0, 1/2-z)$, and $z_{Te} = 5/8$* is not isovectorial with *C7* and cannot account satisfactorily for the observed intensities. In particular, the calculated intensities of the reflections {100} and {200}, whose geometrical structure factors do not contain z, differ very considerably from the corresponding I_o values, the ratios $F_{100}(C27)/F_{100}(C7)$ and $F_{200}(C27)/F_{200}(C7)$ being -0.072 and -0.081, respectively, and thus far from unity. A similar situation is obtained with another conceivable model structure, viz. that based on the structure of the recently described hexagonal NbS_2 (4), even though the nearest-neighbor co-ordination of the metal atom is trigonal prismatic.

The interatomic distances and bond angles in the $MoTe_2$ structure are as follows (Fig. 1):

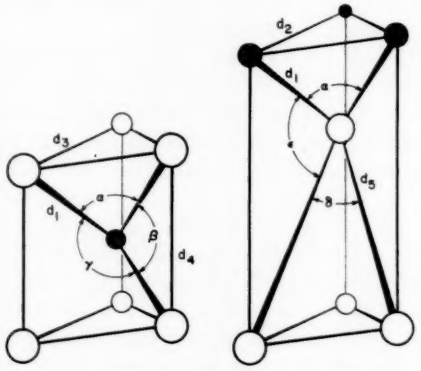

FIG. 1. Nearest-neighbor co-ordination of the molybdenum and tellurium atoms in molybdenum ditelluride. Full circles, molybdenum; open circles, tellurium.

d_1(Mo—Te) = 2.716±12 Å
d_2(Mo—Mo) = d_3(Te—Te) = a_0 = 3.5182±14 Å
d_4(Te—Te) = 3.603±25 Å
d_5(Te—Te) = 3.945±25 Å
d_6(Mo—Mo, between layers) = 7.276±5 Å

α(Te—Mo—Te) = α(Mo—Te—Mo) = 80.74±0.50°
β(Te—Mo—Te) = 83.10±0.60°
γ(Te—Mo—Te) = 135.95±0.60°
δ(Te—Te—Te) = 52.96±0.40°
ϵ(Mo—Te—Te) = 100.59±0.60°.

The Te—Te distance d_5 is about 14% longer than the distance of nearest approach between chains in metallic tellurium, 3.468 Å (19), and the similar Te—Te distance, 3.46±8 Å, in $NiTe_2$(*C6*) (20), but it is fairly close to the Te—Te distance between layers in γ(V, Te)(*C6*), 3.82–3.85 Å (21). The asymmetric Te_I—Te_{II}—Te_I angle between neighboring chains I and II in tellurium which subtends the shortest Te—Te distance in a chain, 2.864 Å, is only 35.4° and thus appreciably smaller than the corresponding angle δ in $MoTe_2$. A symmetric Te_I—Te_{II}—Te_I angle in tellurium is equal to 80.0°, but it subtends not the shortest Te—Te distance but the distance between next-nearest neighbors in the tellurium helix, 4.864 Å. The bond angle δ in $MoTe_2$ is thus almost the arithmetic average of these two bond angles. The Te—Mo—Te angles are very nearly the same as the corresponding S—Mo—S angles in MoS_2(*C7*).

**Origin shifted by (0, 0, 1/4) with respect to the original description of the C27 type as represented by β-CdI_2.*

Since the distances d_3 and d_4 are not equal, the axial ratio of the trigonal prism is not exactly unity, as claimed by Pauling (22, p.175) for molybdenite, but slightly different, $d_4/d_3 = 1.024$.

The shortest Mo—Te distance, d_1, agrees quite well with the sum of the appropriate atomic radii, which is between 2.64 and 2.74 Å, depending on whether the value for Te is taken as the "single-bond" or the "double-bond" radius (22).

Allowing for the fact that WTe_2 is orthorhombic with $b \sim a\sqrt{3}$ (6) and taking the unit-cell dimensions for MoS_2 and WS_2 from (23) and (24), respectively, the square roots of the ratio of the basal areas and the cube roots of the unit-cell volumes are nearly the same for corresponding pairs:

	(basal area)$^{1/2}$	(volume)$^{1/3}$
$(WS_2)/(MoS_2)$	0.998	1.008
$(1/2\ WTe_2)/(MoTe_2)$	1.014	1.009
$(MoTe_2)/(MoS_2)$	1.113	1.121
$(1/2\ WTe_2)/(WS_2)$	1.131	1.122.

Since the estimated radius of Mo in molybdenite is 1.37 Å and that of W in tungstenite is 1.44 Å (22), the difference amounting to about 5%, it is clear that the dimensions of the unit cells of these compounds are determined essentially by the chalkogen atoms.

The stability of $MoTe_2$ on heating under orthobaric conditions is greater than that of WTe_2. There is no isothermal transition between room temperature and 1200° C (cf. (6)). The failure to observe melting in this temperature range is in full agreement with the result of Morette (13), who heated a sample of $MoTe_2$ with excess tellurium *in vacuo* up to 1130° without fusion.

The trigonal-prismatic co-ordination of the molybdenum atom in $MoTe_2$ established in this investigation and the observed diamagnetism of $MoTe_2$ and WTe_2 (13) as well as of MoS_2 throw some doubt on the strong paramagnetism of WS_2 reported for natural material in reference 15. Work is in progress in this laboratory to determine whether MoS_2 and WS_2 form mixed phases; and if so, how the magnetic properties of such phases depend on their composition. It is also intended to re-examine the crystal structure of WS_2 in the light of the conceivable structural ambiguities discussed in the introduction and to obtain a more accurate value for the sulphur parameter than the approximate value of 5/8 first proposed by van Arkel in 1926 (25) and quoted ever since.

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THE PROTON RESONANCE SPECTRA OF SOME SUBSTITUTED FURANS AND PYRROLES[1]

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ABSTRACT

The proton magnetic resonance spectra of some substituted furans and pyrroles have been analyzed for spin coupling constants and chemical shifts.

The relative insensitivity of the spin coupling constants to the nature of the substituent makes it possible to estimate their values in the parent molecules furan and pyrrole. The magnitude of the spin coupling constants is correlated with the angles made by the CH bonds with the CC bonds of the ring.

The chemical shifts are interpreted in terms of an effect due to the electronegativity of the substituent together with the effect due to conjugation with the ring.

The proton resonance spectra of the heterocyclic compounds furan, pyrrole, and thiophene and of their derivatives have been the subject of a number of investigations (1, 2, 3, 4). The present work is an attempt to determine more systematically the effects of substitution on the chemical shifts and spin coupling constants of the ring protons in substituted furans and pyrroles.

These compounds are well suited to a proton magnetic resonance investigation since their spectra are usually capable of a unique interpretation and assignment. The simplest spectra are those of the substituted furans. Here, due to the large difference in the chemical shifts of the α and β protons of the ring, any monosubstituted furan can be classed as an ABX-type spectrum for which a complete analysis is readily achieved. In some cases, where fewer lines are observed than theoretically expected, the spectrum obtained does not give explicit values of any of the coupling constants. This type of spectrum, which is obtained not only for some monosubstituted furans but also for the parent compounds furan and pyrrole, has been the subject of a previous publication (5). The spectra of the substituted pyrroles are complicated by the additional interaction of the N—H proton with the other ring protons. However, a possible interpretation of the spectra of some monosubstituted pyrroles is presented.

EXPERIMENTAL

The compounds used were the commercial samples except for the following. 2-Nitro furan was prepared by nitrating furan with fuming nitric acid and acetic anhydride following the procedure of Marquis (6). 5-Chlormethyl furfural was prepared from sugar and concentrated HCl following the procedure of Aso (7). 3-Furoic acid and its derivatives were kindly supplied by Prof. H. Gilman. The specimen of 2-cyano pyrrole was kindly supplied by Prof. H. J. Anderson.

The spectra of the compounds demonstrated their purity. Only in one case, 2-furoyl-trifluoromethyl ketone, was there any sign of any impurity.

The spectrometer and the techniques for measuring the spectra have been described fully in a previous paper (1). The spectra are shown for 40 Mc/s operation except where stated otherwise, and the convention adopted is that high applied field is positive.

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The Analysis of Spectra

The spectra of the monosubstituted furans studied fall into three distinct classes.

The spectrum of 2-furanmethanethiol (Fig. 1) is given as an example of the type of

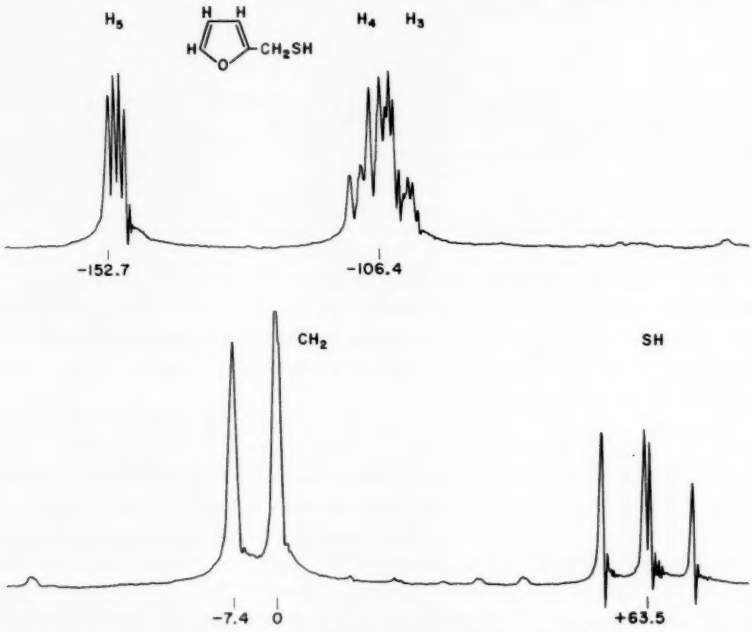


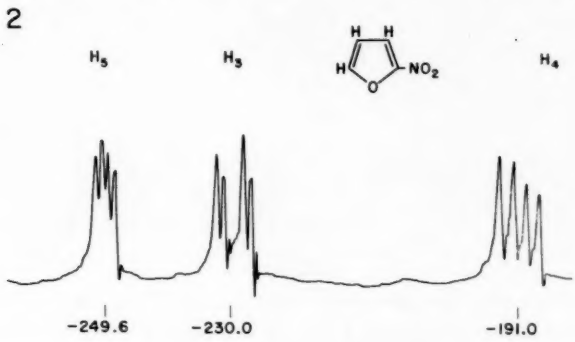
FIG. 1. The proton resonance spectrum of 2-furanmethanethiol (liquid) at 40 Mc/s. (The chemical shifts are in c.p.s. from a dioxane internal reference.)

spectrum obtained from a 2-furfuryl derivative. This is an *ABX* pattern with one of the normal quartets split into 12 unresolved lines by coupling with the CH_2 group. This interaction would be expected to take place between the methylene group and proton 3 of the ring, identifying the H_3 signals. This assignment is confirmed by the chemical shift data, as the methyl mercapto group is electron donating with respect to the furan ring and thus proton 3 would be expected to be more shielded than proton 4.

The spectrum of 2-nitro furan (Fig. 2) demonstrates the influence of a powerful electron-attracting group in position 2 of the ring. The electron shielding of proton 3 is decreased considerably. Thus the signal due to this proton moves to low field to such an extent that the spectrum is a simple first-order one, with the coupling constants given directly by the separations of the lines in each group. Any strongly electronegative group in position 2, e.g., the carbonyl group, gives the same type of spectrum.

The spectrum of 2-furanacrolein (Fig. 3) is an example of the third class of spectrum. Here the ring proton spectrum is very similar to that of 2-nitro furan, but is partially obscured by the side chain spectrum. The assignment shown in Fig. 3 was confirmed by the spectrum of 2-furanacrylic acid, which is identical with the one shown except that in this case the aldehyde splitting of one of the side chain protons is removed leaving a simple quartet.

The remaining spectra are straightforward examples of one of these classes or are



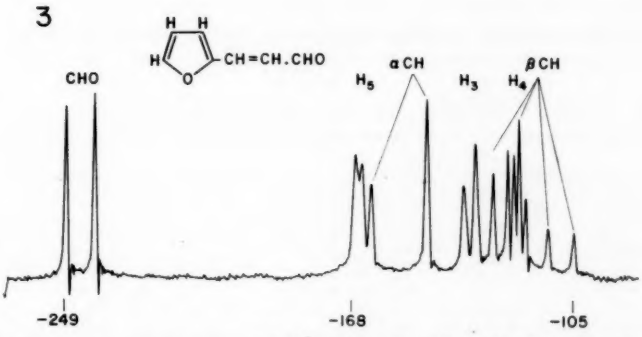


FIG. 2. The proton resonance spectrum of 2-nitro furan (liquid) at 60 Mc/s. The chemical shifts are in c.p.s. from a dioxane internal reference.

FIG. 3. The proton resonance spectrum of 2-furanacrolein in acetone solution at 40 Mc/s. α and β refer to the carbon atoms of the substituent. The chemical shifts are in c.p.s. from a dioxane internal reference.

even more simple spectra, as in the case of the disubstituted furans, and are not reproduced.

The spectra of the 2-substituted pyrroles can be analyzed and assigned in the same general manner as in the furan derivatives; however, there are two additional factors involved. There is the spin coupling of the N—H proton with each of the ring protons which doubles the number of peaks in each spectrum. Also, the chemical shift separation between the α and β protons in the pyrroles is not significantly larger than the change in the chemical shifts due to the substituent group. Thus the assignment of the groups in these spectra is not as certain as the assignments in the furan spectra.

The spectrum of 2-pyrrole aldehyde is shown in Fig. 4. The groups in the spectrum are labelled from left to right, A, B, and X. The problem of the analysis of this spectrum consists in picking out from the observed signals those due to the couplings of the ring protons to the N—H proton and a further coupling of one proton to the aldehyde proton (known to be 1.1 c.p.s. from the doublet separation of the aldehyde proton peak). This process is shown in Table I. The result of this is to leave the three quartets characteristic of an ABX spectrum. The numbering of the lines in these quartets (given in Table I) is unusual due to the fact that J_{AB} is less than J_{AX} or J_{BX}. Apart from this, it is a straightforward ABX analysis (8).

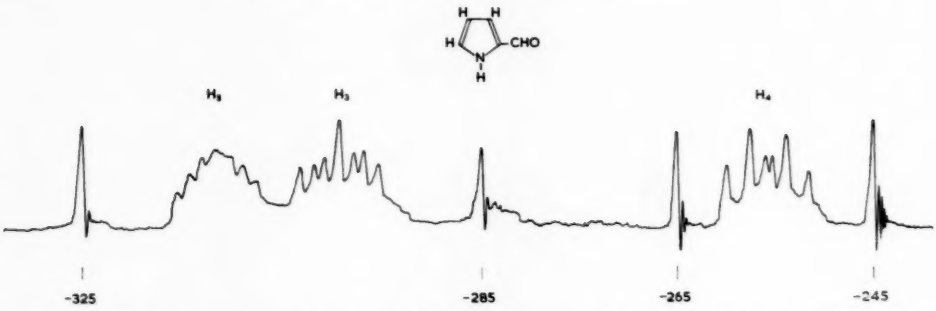


FIG. 4. The proton resonance spectrum of 2-aldehydo pyrrole in acetone solution at 60 Mc/s. The marker side bands are in c.p.s. from the acetone signal.

TABLE I

The analysis of the proton resonance spectrum of 2-pyrrole aldehyde

			A Obs. energy			*B* Obs. energy 12.30+				*X* Obs. energy 55.45+			
			0	1.26			0					0	
			0.63										2.35
			1.26		4.	1.21	1.40	2.42		12.	1.18	2.35	
8.	1.87	2.48	1.88	1.23									
			2.49		2.	2.65	2.42	2.50		11.	3.49	3.92	2.28
6.	3.12	2.47	3.11	1.24									
			3.73				3.90			10.	4.99	4.63	2.14
			4.35										
			Unresolved		3.	5.13	5.37	2.47				6.06	
7.	4.74	(2.45)	4.78							9.	7.19		2.26
			5.40	1.12	1.	6.61	6.37	2.48				8.32	
5.	5.98	2.41	5.96										
			6.52				7.85						
			7.19	1.34									
			7.86										

$J_{A-NH} = 2.45\ (\pm 0.02)$ $J_{A-CHO} = 1.24\ (\pm 0.05)$ $J_{B-NH} = 2.47\ (\pm 0.02)$ $J_{X-NH} = 2.26\ (\pm 0.06)$

The remaining problem is the assignment of the groups in the spectrum. The *X* peak is readily assigned to proton 4 of the ring, from chemical shift and coupling constant data (1). This leaves two possible assignments for the remaining groups. Here the *A* group is assigned to proton 5. This is supported by (*a*) the values of the coupling constants obtained from this assignment agree with the previous values of the coupling constants in the pyrrole ring (1) and with the values of the analogous coupling constants in the furan and thiophene rings (Table IV), and (*b*) the J_{A-CHO} coupling is analogous to the J_{5-CHO} coupling in 2-furfural (1). The effect of the alternative assignment would be to interchange the subscripts 3 and 5 in the δ and J values given for this spectrum.

The analysis of the spectrum of 2-cyano pyrrole (Fig. 5) is very similar to the analysis of Table I, but simpler due to the fact that the J_{5-CHO} coupling is not present. The assignment of the groups in this spectrum also follows the above assignment. In the spectrum of the pure liquid (not shown) the chemical shift difference between protons 3 and 5 is so small that the groups of peaks overlap. This is analogous to the small chemical shift difference in liquid pyrrole and the shift of the α-proton signal to low field with respect to the β-proton signal on dilution in acetone (9). This is further support for the assignment of the low field signal to proton 5.

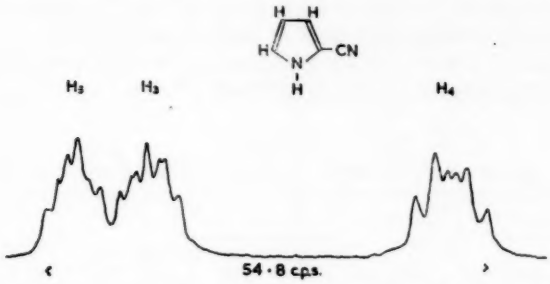


FIG. 5. The proton resonance spectrum of 2-cyano pyrrole in acetone solution at 60 Mc/s.

RESULTS AND DISCUSSION

(a) The Proton–Proton Coupling Constants

The values of the coupling constants which have been derived from the above analyses are shown in Tables II and III, together with the estimated mean deviations. The mean

TABLE II

Proton–proton coupling constants in substituted furans (c.p.s.)

Substance	J_{24}	J_{25}	J_{34}	J_{35}	J_{45}	
2-Methyl furan			3.12(.10)	1.03(.07)	1.90(.08)	$J_{CH_3-3} = 0.91$
2-Furanmethanethiol			3.25	0.73	1.91	$J_{CH_2-3} = 0.79$
2-Furfurylamine			3.18(0.10)	0.76(.10)	1.94(0.10)	$J_{CH_2-3} = 0.84$
2-Furfurol			3.17(.05)	0.84(.07)	1.90(.05)	
2-Furanacrylic acid			3.44(.07)		1.84(.08)	
2-Furanacrolein			3.46(.08)		1.83(.04)	
2-Furamide			3.57(.07)	0.72(.07)	1.76(.04)	
Ethyl 2-furoate			3.47(.09)	0.91(.06)	1.76(.05)	
2-Furoic acid			3.51(.07)	0.86(.09)	1.73(.08)	
Ethyl 2-furoylacetate			3.60(.09)	0.82(.10)	1.72(.05)	
2-Furfural			3.62(.05)	0.82(.06)	1.65(.08)	$J_{CH-5} = 0.81$
2-Nitro furan			3.66(.10)	0.98(.07)	1.92(.07)	
2-Furoyl trifluoromethyl ketone			3.70(.06)	0.76(.06)	1.70(.04)	
2-Furoyl chloride			3.79(.07)	0.79(.07)	1.70(.05)	
5-Chlormethyl furfural			3.67(.07)			
3-Furoic acid	0.8(.1)	1.5(.1)			1.8 (.1)	
2-Methyl-3-furoic acid					1.94(.1)	
4-Methyl-3-furoic acid		1.6(.1)				$J_{CH_3-5} = 1.4$
2,3-Difuroic acid					1.83(.1)	

TABLE III

Proton–proton coupling constants in substituted pyrroles

Substance	J_{13}	J_{14}	J_{15}	J_{34}	J_{35}	J_{45}	
2-Cyano pyrrole	2.25(0.2)	2.42(.2)	2.70(.2)	3.74(.2)	1.45(.2)	2.62(.2)	
2-Aldehydo pyrrole	2.47(.1)	2.26(.1)	2.45(.1)	3.73(.1)	1.36(.1)	2.68(.1)	$J_{CHO-5} = 1.17$
3,4-Dimethyl pyrrole			2.3 (.1)				
2,3,5-Trimethyl pyrrole		2.1 (.1)					

deviations measure the extent to which the line separations, and thus coupling constants, are reproducible in different parts of the spectrum. The mean deviations given in Table II for the substituted furans are solely due to experimental difficulties. The larger values given in Table III are due to an additional error caused by the overlapping of many lines

in each part of the spectrum (e.g. see Figs. 4 and 5), so that the actual positions of the individual lines may not be at the center of the component line.

The average values of the coupling constants in the five-membered ring systems of furan, pyrrole, and thiophene are shown in Table IV. The furan coupling constants are

TABLE IV

Spin coupling constants in five-membered hetercyclic aromatics

Ring system	J_{12} (=J_{15})	J_{13} (=J_{14})	J_{23} (=J_{45})	J_{24} (=J_{35})	J_{34}	J_{25}
Furan	2.43 (.16)	2.43 (.24)	1.80 (.09)	0.80 (.10)	3.53 (.13)	1.55 (.1)
Pyrrole			2.63 (.03)	1.44 (.05)	3.42 (.42)	
Thiophene			5.2 (.3)	1.3 (.3)	3.6 (.3)	2.7 (.3)

the mean of the results of Table II, the pyrrole coupling constants the mean of the results of Table III and reference 1, and the thiophene coupling constants the mean of the values obtained from the analysis of the thiophene spectrum (10) and those obtained from substituted thiophenes (4).

Considering first the results given in Tables II and IV for the substituted furans. The spin coupling constants are in agreement with the less accurate results of reference 1 and also with the less extensive measurements of Leane and Richards (3). The average values of the coupling constants in the furan ring are also fully consistent with the observed furan spectrum and the 2-furfural 40 Mc/s spectrum (5). The results for the 2-substituted furans of Table II, however, do show one striking feature. Although the variations in the magnitudes of the coupling constants J_{25} and J_{45} are not significantly greater than the experimental error, the magnitude of the coupling constant J_{34} changes markedly over a range of substituent groups. The 2-substituted furans in Table II are listed in the order of increasing "electronegativity" of the substituent group (as determined by the ring proton chemical shifts (see Table V)). It can be seen that, although the total

TABLE V

Coupling constants (c.p.s.) and angles (degrees) in unsaturated cyclic compounds

	θ_2	θ_3	$\theta_2+\theta_3$	J_{23}	ref. for θ_1, θ_2	θ_1	$2\theta_1$	J_{34}
Furan	126	134	260	1.8	*a*	128	256	3.5
Pyrrole	126	$131\frac{1}{2}$	$257\frac{1}{2}$	2.6	*b*	$126\frac{1}{2}$	253	3.4
Thiophene	$124\frac{3}{4}$	$127\frac{1}{2}$	$252\frac{1}{4}$	5.2	*c*	$123\frac{1}{2}$	247	3.6
Ethylene	120	120	240	11	*d*			
		Hydrocarbons	2θ	J				
5 members			252	3	*e*			
6 members			240	7	*e*			
7 members			231.4	11	*e*			

a. B. Bak, L. Hansen, and J. Rastrup-Hansen. Discussions Faraday Soc. **19**, 30 (1955).
b. B. Bak *et al.* J. Chem. Phys. **24**, 720 (1956).
c. B. Bak *et al.* J. Chem. Phys. **25**, 892 (1956).
d. θ taken as 120°. Coupling constant from ref. 8 p. 242.
e. Coupling constant from ref. 8 p. 193.

variation of J_{24} is only of the order of 0.5 c.p.s., there is a close correlation between the magnitude of J_{34} and the "electronegativity" of the substituent group. The measurements on substituted pyrroles (Table III and ref. 1) support this correlation, but since the experimental error is much larger in this case and only a few compounds have been measured, this effect is not seen so clearly.

One more point that might be enlarged upon is the magnitude of the coupling constants J_{23} and J_{34} in the various heterocyclic rings. The angular dependence of the gem coupling constants (11) suggests that there may be a correlation between the sum of the angles $\theta_1+\theta_2$ and the H—H coupling constant J_{34}, and $\theta_2+\theta_3$ with J_{23} (see Fig. 6). Further, this

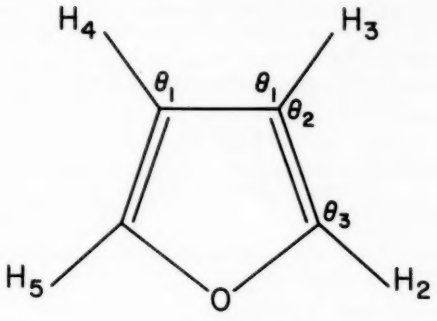


FIG. 6.

correlation might be expected to be different for the two types of coupling constants since J_{23} operates through essentially a double bond (of length 1.35 Å) whereas J_{34} operates over a 'single' bond (of length ~1.44 Å).

In Table V the values of the coupling constants are shown along with the angle sums for coupling constants acting through double bonds, 'single' bonds, and aromatic bonds. The angle θ for the hydrocarbons was calculated on the assumption that the 5-, 6-, and 7-membered rings are regular polygons. These data are plotted in Fig. 7 showing the rather good correlation with the angle sum.

A further point of interest is the interaction between the side-chain protons and the ring protons. It can be seen from Tables II and III that in all cases except 2-furfural and 2-aldehydo pyrrole the side chain protons couple with the neighboring ring proton.

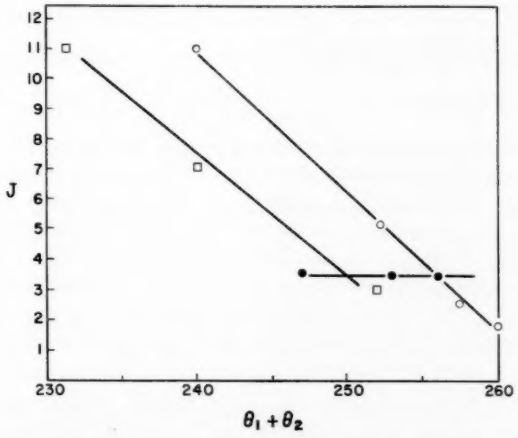


FIG. 7. The relation between spin coupling constant and angle sum. ○ CC length 1.35 Å (double bond). ● CC length ~1.43 Å ('single' bond). □ CC length ~1.40 (aromatic CC bonds).

Thus the apparent coupling of the aldehyde proton to proton 5 of the ring is rather remarkable. There are, however, further experimental facts in this case, in particular there is a change in the fine structure of the signal due to proton 5 of the ring on going from 30 Mc/s (3) to 40 Mc/s (1). Thus this effect may not be a straightforward long-range coupling interaction of the same type as that observed in substituted thiophenes (12). However, more data is necessary before this question can be answered.

(b) The Ring-Proton Chemical Shifts

The results of the chemical shift measurements are shown in Tables VI and VII. The

TABLE VI

Substituent effects in the ring-proton chemical shifts of furans
(Results are given in parts per 10^7)

Compound	(a) Pure liquids			(b) In 10% acetone solution				(c) 10% CH_2Cl_2 solution		
	δ_2	δ_4	δ_5	δ_2	δ_3	δ_4	δ_5	δ_2	δ_4	δ_5
2-Methyl furan	+3.8	+0.8	+1.0	—	+4.35	+1.53	+2.05	+4.3	+1.5	+2.3
2-Furanmethanethiol	+1.5	+0.3	+0.3	—						
2-Furfurylamine	+1.3	−0.5	−0.8	—	+2.42	+1.00	+1.37			
2-Furfurol	−0.4	−0.1	−0.5	—	+1.51	+0.76	+0.89	+1.5	+1.5	+0.5
Furan	0.0	0.0	0.0	0.0	0.00	0.00	0.00	0.0	0.0	0.0
2-Furanacrylic acid				—	−4.08	−1.44	−1.36			
2-Furanacrolein				—	−5.51	−2.09	−2.26			
Ethyl furoate	−8.5	−1.8	−3.3	—	−7.74	−1.83	−2.26			
2-Furoic acid				—	−7.95	−1.81	−2.20	−8.8	−1.0	−0.8
Ethyl 2-furoylacetate	−11.3	−3.5	−3.3	—	−9.59	−2.55	−2.98			
Furfural	−11.0	−3.5	−4.8	—	−9.87	−2.94	−3.66	−8.3	−1.5	−2.3
2-Nitro furan	−10.8	−4.3	−3.3	—	−10.65	−4.02	−3.18			
2-Furoyl trifluoromethyl ketone				—	−11.98	−3.73	−4.54			
2-Furoyl chloride	−12.0	−3.8	−4.8	—	—	—	—			
5-Chloromethyl furfural	−11.0	−4.5	—	—	—	—	—			
2,5-Dimethyl furan	+5.0	+5.0	—	—			—			
3-Furoic acid*				−7.0	—	−3.9	−1.7			
2-Methyl-3-furoic acid*				—	—	−2.9	+0.8			
4-Methyl-3-furoic acid*				−5.2	—	—	+2.0			
2,3-Difuroic acid*				—	—	−6.4	−4.2			

(a) Actual furan value −38.3 (α protons); −27.5 (β protons).
(b) Actual furan value −54.82 (α protons); −43.58 (β protons).
*Unknown concentration, very dilute; experimental error ±0.3.

TABLE VII

Ring-proton chemical shifts of substituted pyrroles

Compound	δ_2	δ_4	δ_5
2-Methyl pyrrole	+3.58	+1.75	+2.06
Pyrrole	0.00	0.00	0.00
2-Cyano pyrrole	−7.47	−1.42	−3.31
2-Aldehydo pyrrole	−8.87	−1.95	−4.56

NOTE: All compounds measured in 10% solutions in acetone, with the solvent peak as reference. Results are in parts per 10^7. Actual pyrrole values are −47.08 (α protons), −40.43 (β protons).

chemical shifts are given in parts per 10^7 from the chemical shift of the corresponding proton in the parent compound furan and pyrrole. These chemical shift differences will be designated by δ values in the following discussion.

Table VI gives the results for the substituted furans. Three series of measurements are given. The first set of results (Table VI*a*) was determined by measurements at 40 Mc/s on the pure liquid samples using an internal dioxane reference. They are accurate to ± 1 c.p.s. i.e. to ± 0.3 parts per 10^7. In the second set (Table VI*b*) the compounds were remeasured (at 60 Mc/s) in 10% solutions in acetone, using the acetone signal as reference. From three independent spectra for each solution, the reproducibility of the latter results was ± 0.2 c.p.s. i.e. ± 0.03 parts per 10^7. Also in Table VI*c* are given some measurements of Corey *et al.* (2) using CH_2Cl_2 as solvent.

The three sets of results in Table VI provide a means of estimating the effect of dilution (in acetone) on the δ values and also how the δ values change in different solvents. A comparison of the δ values of the compounds in acetone (VI*b*) and the pure liquids (VI*a*) shows that there is a constant shift to high field in the former case, of 0.9 ± 0.5 parts per 10^7 and this shift is the same for protons 3, 4, and 5 of the ring and is nearly independent of the substituent group. This shows that dilution in acetone does not give rise to a significant change in the internal δ values for these compounds. This is probably due to the fact that the environment of a substituted furan molecule in the pure liquid state is very similar to the environment of the same molecule in acetone. However, when the δ values in the two very different solvents acetone and dichloromethane are compared (Tables VI*b* and VI*c*), a different result is obtained. Here the differences in the δ values depend markedly on the substituent group. For 2-methyl furan and 2-furfurol there is reasonably good agreement but there are larger differences of about 1.5 parts in 10^7 for 2-furfural and 2 furoic acid. This is to be expected since the COOH and CHO groups give rise to much larger δ values than the CH_3 or CH_2OH groups and thus changes due to different solvents would give larger absolute changes in the δ values. It is evident then that the effect of the substituent group on the ring-proton chemical shifts is to some extent a function of the solvent used (13). Further, the chemical shift of proton 3 could be influenced by different neighboring anisotropic effects due to the different substituents. A discussion of the relative chemical shifts of H_3, H_4, and H_5 with substitution can therefore at best be roughly qualitative.

From the data for the 2-substituted furans in acetone (Table VI*b*) the chemical shifts are found to be linearly related. That is

$$\delta_3 = 3.08\delta_4 - 0.42 \text{ with a mean deviation of } \pm 0.8 \times 10^7,$$

$$\delta_5 = 1.23\delta_4 + 0.10 \text{ with a mean deviation of } \pm 0.1 \times 10^7.$$

This implies that the effect of substitution is different from that in a benzene ring where the *m* signals are chiefly due to inductive effects and the *o*, *p* to resonance effects. This difference could arise because in the parent molecule furan, the resonance effect influences *both* the α and β positions (14). The effect of substitution in 5-membered rings is twofold. Firstly, the substituent (due to the electronegativity difference between it and H) tends to shift all signals to low field if more electronegative than H, the closest proton being shifted most and the effect being attenuated as the distance from the substituent increases. Secondly, because of its power to donate or withdraw electrons from "aromatic" rings the substituent can cause the signals to move to high field or low field respectively. Again, the largest effect is felt by the proton closest to the substituent. This mesomeric effect probably behaves in a fashion analogous to that in the parent compound affecting all positions in the same qualitative way (that is, all increase in π-electron density or all decrease). This is consistent with the linear dependences of δ_3, δ_4, and δ_5. Semi-

quantitatively, we may distinguish between the effect of electron-donating and -withdrawing substituents. In the case of the former, the electronegativity of the substituent shifts the signals to low field but the mesomeric effect increases the π-electron density causing greater shielding, which causes the signals to appear at higher field. In the case of electron-withdrawing substituents, however, both the electronegativity and mesomeric effects operate to shift the signals to low field. We expect therefore for 2-methyl furan, where the electronegativity effect is small, that the donor property of the methyl group will cause high field shifts relative to furan. Since all of the substituents used here are more electronegative than CH_3, we expect for the donors (e.g. NH_2, OH) that the shifts will be at lower field than in 2-me-furan, and, as one progresses to electron-withdrawing substituents, that the proton signals appear at increasingly low fields. This is indeed the order of the chemical shifts data given in Table VI*b*. Also as anticipated, the largest changes are exhibited by δ_3. The less complete results for the 2-substituted pyrroles seem to show a similar behavior of the effect of substitution on chemical shift.

It is of interest also to note that the effect of multiple substitution is very nearly additive. For example, if the chemical shifts relative to furan for a $2-x$-substituted furan are δ_{3x}, δ_{4x}, δ_{5x} and for $3-y$, are δ_{4y}, δ_{5y} then for the $2-x$, $3-y$-disubstituted furan the shifts are $\delta_{4x}+\delta_{4y}$ for H_4 and $\delta_{5x}+\delta_{5y}$ for H_5. For example, the calculated shifts for 2,3-difuroic acid are $\delta_3=\delta_5=-5.7$ and $\delta_2=\delta_4=-3.9$, and the observed shifts are -6.4 and -4.2 respectively. Similarly the calculated shifts for 2-methyl-3-furoic acid are $\delta_3=\delta_5=-2.4$ and $\delta_4=\delta_5=+0.4$, which may be compared with the observed shifts of -2.9 and 0.8 respectively.

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THE ELECTRICAL CONDUCTIVITY OF LIQUID TIN (II) SULPHIDE[1]

DENIS BOUTIN AND MARCEL BOURGON

ABSTRACT

The electrical conductivity "σ" of tin (II) sulphide in the liquid state has been measured using a capillary type cell. Both a-c. and d-c. methods were used. The conductivity of SnS increases regularly with temperature, from approximately 24 $ohm^{-1}\,cm^{-1}$ at 895° C to 31.2 $ohm^{-1}\,cm^{-1}$ at 930° C. The similarity of results obtained with both a-c. and d-c. methods, the positive temperature coefficient of conductivity, the high value of the conductivity and the absence of electrolysis effects when passing heavy currents in the melt lead to the conclusion that SnS remains a semiconductor in the liquid state. The value of the energy gap has been calculated to be 1.9 ev for the liquid as compared to the value 1.2 ev for the solid. Conductivity measurements have been limited to the temperature of approximately 935° C because of the decomposition of SnS at higher temperatures.

INTRODUCTION

Study of the electrical properties of liquid inorganic salts and oxides has shown that these chemical compounds are often ionic in the liquid state as evidenced by the high value of the conductivities, the positive temperature coefficients of conductivity, and the high current efficiencies (1, 2, 3). The electrical conductivity of a few metallic sulphides in the liquid state has been investigated: NiS (9), Bi_2S_3 (9), and FeS (4, 5, 7) have been reported to behave as typical metallic conductors while Cu_2S (4, 5, 6) and Tl_2S (10) have been shown to be semiconductors. Liquid antimony (III) sulphide Sb_2S_3 has a mixed conductivity, ionic and electronic (8).

Tin (II) sulphide SnS is known to be a semiconductor in the solid state (11) and has been reported to possess mixed conductivity in the liquid state (9). In order to determine whether this compound retains its semiconductivity in the liquid state it was planned to study its electrical conductivity more thoroughly than was done by previous workers.

EXPERIMENTAL

Preparation of SnS

The tin (II) sulphide used in this study was prepared by direct synthesis from the elements: "Reagent" grade tin and recrystallized sulphur were used. The tin sulphide so obtained contains free sulphur and some SnS_2. Consequently, the crude sulphide was heated under vacuum at 450° C to eliminate the free sulphur and melted under a nitrogen atmosphere at 1000° C, this temperature being maintained between 1 and 2 hours in order to decompose the tin (IV) sulphide to tin (II) sulphide and sulphur. The furnace temperature was then brought down to 890° C and a partial vacuum was maintained over the melt to eliminate the last traces of sulphur. The tin (II) sulphide was then distilled at the same temperature under high vacuum using a graphite condenser. The tin (II) sulphide thus prepared has a metallic appearance and is completely soluble in concentrated HCl. Two batches of sulphide were prepared and showed identical X-ray powder patterns (114.8-mm camera, Cu radiation, Ni filter): these patterns were strictly identical with the known X-ray powder pattern of SnS (12). The characteristic X-ray

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Contribution from the Department of Chemistry, University of Montreal, Montreal, Que. This paper was taken from the thesis of D. Boutin, presented in partial fulfillment of the requirements for the degree of M.Sc., May 1960. Presented at the 43rd Annual Conference, Chemical Institute of Canada, Ottawa, Ontario, June 1960.

lines of SnS_2 and SnO_2 were absent from the X-ray diagrams. The first batch was nevertheless rejected because chemical analysis showed it to contain graphite particles. The second batch was analyzed for tin using the potassium iodate method: found $78.58 \pm 0.05\%$, theoretical 78.73%. According to the analysis figure the tin sulphide used in this study, although very near the stoichiometric composition, is slightly enriched in sulphur.

The Conductivity Cell

The cell used for measuring the electrical conductivity was of the capillary type and is shown in Fig. 1. It is made entirely of "Vitreosil" tubing and has four electrodes made

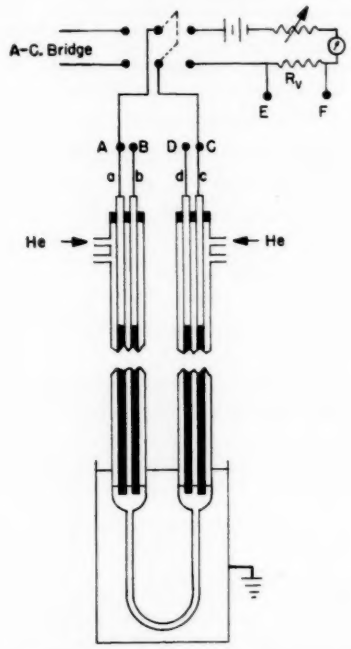

FIG. 1. Cell for measuring the electrical conductivity.

of spectrographic graphite rods: two of these electrodes carry current into the melt and the two others serve as potential probes, this system having the advantage of eliminating lead resistances. The cell is approximately 50 cm long and the over-all length of the capillary tube is approximately 10 cm. In order to obtain good temperature control and to eliminate stray currents in the melt the cell was placed in a liquid tin bath which was connected to ground. The cell and the liquid tin bath were contained in a "Mullite" tube which, in turn, was placed in a furnace heated by means of silicon carbide rods and controlled by a Weston Celectray Controller. Temperature measurements were made by means of calibrated Pt, 10% Rh–Pt thermocouples. The measuring thermocouple was contained in a sheath made of pure recrystallized alumina and placed between the two tubes of the cell so that the junction was in the middle of the capillary portion of the cell. Provisions were made to introduce purified helium gas into the cell. Because

of the rather high vapor pressure of tin (II) sulphide the helium gas was not circulated in the cell but a slightly positive static atmosphere was maintained over the melt.

The measuring cells were calibrated at room temperature using 0.1 *N* KCl. The cell constants were determined using an a-c. bridge operated at 1000 cycles/sec (13). With cells having a 10-cm-long capillary (I.D. 1 mm or lower) cell constants as high as 1200–1500 were obtained.

Resistance Measurements

Two methods were used to measure the resistance of the melt: a direct-current method and an alternating-current method. With the d-c. method the potential drops were measured across the potential probes of the cell and across a calibrated resistance in series with the latter using a potentiometer. By this method the lead resistances are eliminated.

The a-c. measurements were made using the same bridge as was used for calibrating the cells. This bridge measures the resistance of the melt and the resistance value thus found includes the resistance of the leads. A correction was made for the lead resistances at the different temperatures by using the following procedure.

Referring to Fig. 1, the d-c. potential drops across AC, BD, and EF are respectively:

$$E_{AC}=(R_x+r_a+r_c)i, \quad [1]$$

$$E_{BD}=R_x i, \quad [2]$$

$$E_{EF}=R_v i \quad [3]$$

where R_x, r_a, and r_c are the resistances of the melt and the electrodes respectively and R_v is the standard resistance in series with the cell. The d-c. resistance between points A and C is thus:

$$R_{AC}=R_x+r_a+r_c=R_v.\ E_{AC}/E_{EF}. \quad [4]$$

The d-c. resistance of the melt is given by:

$$R_x=R_v.\ E_{BD}/E_{EF}. \quad [5]$$

The difference between [4] and [5] gives the resistance of the electrodes:

$$r_a+r_c=R_v(E_{AC}-E_{BD})/E_{EF}. \quad [6]$$

The a-c. resistance across points A and C as measured by the bridge is:

$$R'_{AC}=R_x+r_a+r_c+r \quad [7]$$

where r is the residual resistance of the bridge and was found to be 0.4 ohm. The a-c. resistance of the melt R″ is thus given by [7]−[6].

RESULTS

Typical curves obtained by measuring the conductivity of liquid tin (II) sulphide as a function of temperature are shown in Fig. 2. Curve A shows the results obtained while increasing the temperature; curve B gives the conductivity values of the same sample obtained while decreasing the temperature from a maximum of approximately 1050° C. Curve C was obtained using a different sample and a different cell while decreasing the temperature: all these results were obtained by means of d-c. measurements. It is noticeable that the results obtained while decreasing the temperature are always

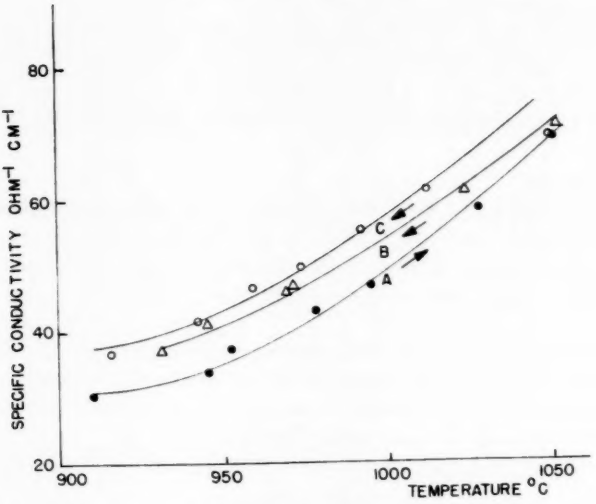

FIG. 2. Specific conductivity of liquid SnS as a function of temperature.

higher than those obtained while increasing the temperature. It is to be noticed also that curves B and C do not coincide and this could be due to the non-reproducibility of the different cells. This latter point was checked by mounting two cells with identical samples in the furnace so that both of them would follow the same thermal program. Conductivity measurements were made while increasing and decreasing the temperature and although the conductivity values obtained during the cooling cycle were, as in earlier experiments, higher than those obtained during the heating cycle the conductivity values obtained while decreasing the temperature were identical in both cells.

The different values of the conductivity obtained when heating or cooling the sample could be due to an increase in the tin content of the melt during the heating cycle. This increase in the tin content could be due to a reduction of the SnS by the graphite electrodes, to a partial electrolysis of the melt caused by the direct current or to the decomposition of the SnS. The first of these hypotheses was verified by heating SnS samples in closed quartz tubes for a few hours at approximately 1050° C; one of the tubes contained in addition a piece of the graphite used for electrodes. After the experiment sulphur deposits could be seen in the upper parts of both tubes showing that SnS does decompose independently of the presence of carbon.

To determine the decomposition temperature it was planned to do conductivity measurements as a function of time. To determine also whether there was partial electrolysis of the melt when using direct current the circuit permitting simultaneous a-c. and d-c. measurements and described in the experimental section was set up.

The results of these experiments are shown in Table I and Fig. 3 where the specific conductivity of the melt is shown as a function of time at several temperatures. Many such time–conductivity curves were determined on different samples in different cells: in the preliminary runs the heating time was extended for at least 30 hours at each temperature. The curves shown in Fig. 3 are those obtained under the best experimental conditions. The same cell was used throughout but because of the volatilization of the

TABLE I

Conductivity of tin (II) sulphide

Time, hours	T, °C	R'_{AC}, ohms	R_{AC}, ohms	R_X, ohms	$R_{AC}-R_X$, ohms	R'', ohms	σ, $ohm^{-1}\,cm^{-1}$
0	894	41.1	40.63	40.12	0.51	40.2	23.90
4.0	896	41.0	40.50	39.98	0.52	40.1	23.99
14.0	895	41.1	40.54	40.03	0.51	40.2	23.96
18.0	895	41.1	40.52	40.00	0.52	40.2	23.98
0	908	37.1	36.59	36.08	0.51	36.2	26.58
5.5	907	37.0	36.52	36.01	0.51	36.1	26.64
8.8	908	37.1	36.61	36.07	0.54	36.2	26.59
18.0	907	37.0	36.50	36.00	0.50	36.1	26.64
21.0	907	37.0	36.56	36.04	0.52	36.1	26.61
0	915	35.0	34.48	33.96	0.52	34.1	28.24
1.0	916	34.8	34.31	33.82	0.49	33.9	28.36
1.8	915	35.0	34.38	33.87	0.51	34.1	28.31
4.5	915	35.0	34.48	33.99	0.49	34.1	28.21
8.5	916	34.9	34.30	33.81	0.49	34.0	28.36
0	930	31.6	31.16	30.70	0.46	30.7	31.24
12.3	929	31.7	31.35	30.85	0.50	30.8	31.08
13.5	930	31.5	31.13	30.65	0.48	30.6	31.29
14.5	930	31.5	31.08	30.61	0.47	30.6	31.33
0	937	29.7	29.22	28.76	0.46	28.8	33.36
4.3	939	29.3	28.73	28.29	0.44	28.5	33.90
23.8	938	29.1	28.52	28.07	0.45	28.2	34.16
24.5	939	28.9	28.45	27.98	0.47	28.0	34.27
48.5	944	19.8	x	x	x	x	x

Sulphur deposited at top of the cell.

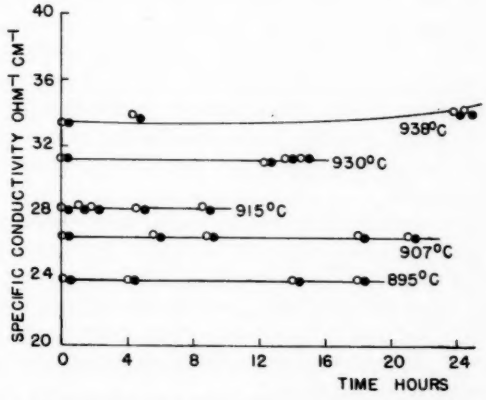

FIG. 3. Specific conductivity of liquid SnS as a function of time at constant temperature. ● a-c. data. ○ d-c. data.

sample additional SnS was added periodically. It was found necessary to bubble helium through the melt before each measurement in order to obtain reproducible results.

As can be seen from the curves an increase in the conductivity of the melt as a function of time occurs at a temperature of approximately 938° C. This is attributed to an increase in the tin content due to the decomposition of the tin sulphide. After completing the measurements the cell was maintained at a few degrees above the decomposition temperature for many hours at the end of which period the conductivity had increased to the point where it was difficult to measure: determination of the tin content of the melt

at the completion of the experiment showed that the latter had increased from 78.58 to 79.80%. The decomposition temperature was reproducible from sample to sample within 3 or 4 degrees. Resistance measurements made at temperatures higher than the decomposition temperature, using uncalibrated cells, showed that the decomposition rate increased as the temperature increased. In all cases sulphur deposition could be observed in the cooler parts of the cell.

The curves plotted in Fig. 3 show the results obtained with both alternating and direct currents. The conductivity values given in Table I are those calculated from the d-c. measurements, which are thought to be more precise. There is a small difference between the resistance values obtained with alternating current as compared with those obtained with direct current: this is probably due in part to a certain uncertainty in the residual resistance of the a-c. bridge and we do not believe it to be significant.

Electrolysis experiments were made on liquid SnS using a graphite crucible which served as the cathode and a graphite rod enclosed in a quartz tube which served as the anode. These experiments were made at 910° C using heavier currents (approximately 2 amperes) than were employed during the conductivity measurements. Preliminary experiments showed that it was difficult to distinguish the tin, which could be produced by electrolysis, from the tin sulphide. The anode compartment was instead observed for signs of sulphur evolution: there was no sulphur deposit in the cool part of the quartz tube even after the current had been passed for 2 hours.

DISCUSSION

Delimarskii and Velikanoff (9) have reported values for the conductivity of liquid SnS; their values range from 69 $ohm^{-1}cm^{-1}$ at 900° C to 103 $ohm^{-1}cm^{-1}$ at 1000° C with a temperature coefficient of 3.8×10^{-3}. They conclude from these results that liquid SnS has a mixed conductivity, ionic and electronic. The high results obtained by these workers are most probably due to the contamination of the melt by metallic tin: they prefused their sulphide at a probably too high temperature as evidenced by the stated analytical figures: they report an initial tin content of 79.7%, which increased to 80.6% at the end of the measurements.

Our results show that the conductivity of liquid tin (II) sulphide increases from approximately 24 $ohm^{-1}cm^{-1}$ at 895° C to 31.2 $ohm^{-1}cm^{-1}$ at 930° C with a temperature coefficient of 6.5×10^{-3}. The conductivity of SnS is somewhat high to be due to the migration of ions under the influence of an electric field. The absence of a considerable amount of ions is indicated by the fact that the d-c. and a-c. values of the conductivity are identical within experimental errors. The absence of sulphur evolution during the electrolysis experiments corroborates these conclusions.

Anderson and Morton (11) have shown SnS to be a semiconductor in the solid state. The conductivity follows the law:

$$\sigma = A_1 \exp(-E_1/kT) + A_2 \exp(-E_2/kT)$$

where the first term is preponderant at low temperatures and is attributable to an excess of non-metal in the lattice (*p*-type semiconduction) while the second term takes importance at high temperatures and is attributed to the intrinsic conduction of the lattice. From the high-temperature term, Anderson and Morton have calculated the width of the forbidden energy gap for intrinsic conduction to be 1.2 ev. These workers also showed that solid SnS can act as a *n*-type semiconductor when treated by hydrogen at high temperature, this operation having the effect of increasing the tin content.

The conductivity values of liquid tin sulphide plotted in Fig. 3 have been replotted in Fig. 4 as a function of the inverse of the absolute temperature to give a straight line.

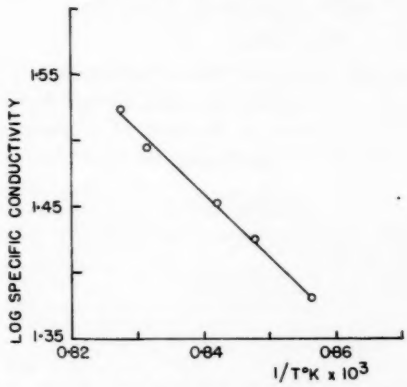

FIG. 4. Log specific conductivity as a function of the inverse of the absolute temperature for liquid SnS.

This line follows the law:

$$\sigma = A \exp(-E/kT).$$

All the facts stated above lead to the conclusion that tin (II) sulphide remains a semiconductor in the liquid state. The width of the forbidden energy gap as calculated from the slope of the line in Fig. 4 is 1.9 ev.

Attempts were made to determine the change in conductivity of SnS as it passes from the liquid state to the solid state. Although the cell design did not permit quantitative estimation of the conductivity, it was observed, in many cases, that the resistance of SnS increases sharply at the freezing point. Comparison of our results for the liquid state with the high-temperature results obtained by Anderson and Morton (11) for the solid state also indicates a sharp decrease of the conductivity at the freezing point.

It should be mentioned that the tin (II) sulphide used in this study is slightly richer in sulphur then the stoichiometric compound. One way of determining the influence of this excess sulphur on the conductivity would be to measure the conductivity of SnS as a function of sulphur pressure using hydrogen – hydrogen sulphide atmospheres: this is somewhat difficult because of the volatility of the tin sulphide.

Besides the liquid semiconductors mentioned in this paper other occurrences of semiconductivity in liquids have been reported. By measuring the electrical conductivity and the thermoelectric power of liquid selenium Henkels and Maczuk (14, 15) have shown this elementary substance to be a semiconductor in the liquid state with a forbidden energy gap of 2.31 ev as compared to 1.8 ev for the solid. Epstein, Fritzsche, and Lark-Horovitz (16, 17, 18) have measured the electrical conductivity, the thermoelectric power and the Hall coefficient of pure tellurium at the melting point and in the liquid state: they find a sharp decrease in conductivity on passing from the liquid to the solid state. Their experimental results indicate that the semiconducting properties persist in the liquid state and that a graded transition to metallic properties takes place at higher temperatures. Inouye, Tomlinson, and Chipman (19) conclude, from conductivity measurements, that FeO remains a semiconductor in the liquid state. Liquid HgSe (20)

has been reported to be a semiconductor with an energy gap of 2.3 ev. Ioffe (10) has reported the compounds Sb_2O_3, Bi_2O_3, Na_2Te_3, Na_2Te_6 to be semiconductors in the liquid state.

ACKNOWLEDGMENTS

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TETRAHYDROFURANS

I. 2,2-DIMETHYL-4-SUBSTITUTED-4-HYDROXYMETHYLTETRAHYDROFURANS AND RELATED COMPOUNDS[1]

B. K. Wasson, C. H. Gleason, I. Levi, J. M. Parker, L. M. Thompson, and C. H. Yates

ABSTRACT

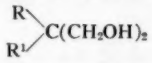
Substituted methallylmalonic esters (I) were reduced with lithium aluminum hydride to the corresponding 2-methallyl-1,3-propanediols (II). These diols II underwent cyclization on treatment with a mineral acid to the isomeric 2,2-dimethyl-4-substituted-4-hydroxymethyltetrahydrofurans (IV). II and IV were converted to the respective carbamates III and V, which exhibited pharmacological activity. The assigned structures of the cyclic compounds IV were proved by infrared analyses and the following transformations. Ring scission of 2,2-dimethyl-4-allyl-4-hydroxymethyltetrahydrofuran (IV*e*) with acetic anhydride – pyridine hydrochloride yielded 2-allyl-2-methallyl-1,3-propanediol diacetate (X*e*). Catalytic reduction of IV*e* gave 2,2-dimethyl-4-*n*-propyl-4-hydroxymethyltetrahydrofuran (IV*d*). Reductive cleavage of the tosylate VIII*b* of 2,2,4-trimethyl-4-hydroxymethyltetrahydrofuran (IV*b*) with lithium aluminum hydride yielded the known 2,2,4,4-tetramethyltetrahydrofuran (IX*b*).

While preparing 2,2-disubstituted-1,3-propanediol dicarbamates, it was noted that an intermediate, 2-allyl-2-methallyl-1,3-propanediol (II*e*), was labile to hydrochloric acid affording a compound assumed to be 2,2-dimethyl-4-allyl-4-hydroxymethyltetrahydrofuran (IV*e*). This assignment, made by analogy with a known method of preparing tetrahydrofurans (1–3), was subsequently verified. Since IV*e* possessed interesting pharmacological activity it was decided to prepare additional 2,2-dimethyl-4-substituted-4-hydroxymethyltetrahydrofurans (IV). Thus substituted methallylmalonic esters (I) were reduced to the corresponding 2-substituted-2-methallyl-1,3-propanediols (II) and subsequently cyclized by means of mineral acid. Both II and IV were converted to the corresponding carbamates III and V (Fig. 1).

Substituted methallylmalonic esters (I) were reduced by lithium aluminum hydride (4) to 2-substituted-2-methallyl-1,3-propanediols (II) (Table I). The use of sodium and

TABLE I

Substituted-1,3-propanediols



No.	R	R^1	% Yield	B.p. °C	B.p. mm
XI	H	$CH_2CH{=}CH_2$	73.5	110–112°	5
II*a*	H	$CH_2C(CH_3){=}CH_2$	74.4	75–83°	0.2–0.3
II*b*	CH_3	$CH_2C(CH_3){=}CH_2$	92.3	137–143°	27–30
II*c*	CH_2CH_3	$CH_2C(CH_3){=}CH_2$	75.0	140–147°	15–20
II*d*	$CH_2CH_2CH_3$	$CH_2C(CH_3){=}CH_2$	87.8	121–154°	15–16
II*e*	$CH_2CH{=}CH_2$	$CH_2C(CH_3){=}CH_2$	81.8	151–156°	14–15
II*f*	$CH_2C{\equiv}CH$	$CH_2C(CH_3){=}CH_2$	95.6	84–104°	0.05–0.10
II*g*	C_6H_5	$CH_2C(CH_3){=}CH_2$	61.6	128–141°	0.27–0.50

[1]*Manuscript received May 4, 1960.*
Contribution from the Research Laboratories, Charles E. Frosst & Co., Montreal, Quebec.

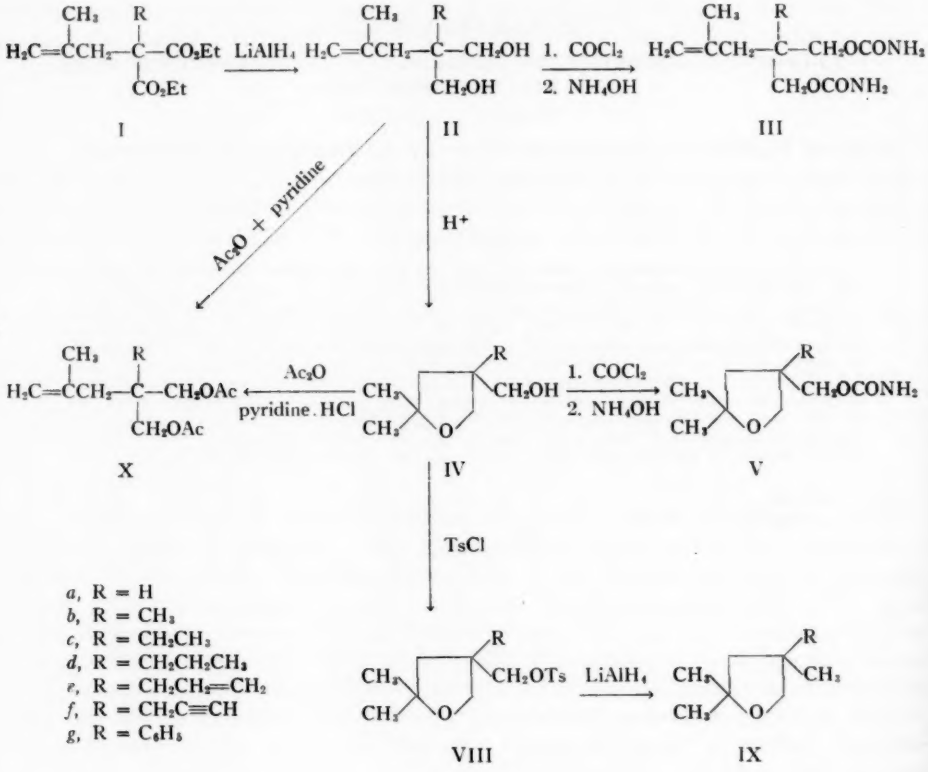


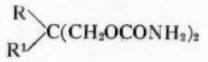
FIG. 1.

an alcohol (ethanol, 1-propanol, 1-butanol) (5) was unsatisfactory. Decomposition of the excess hydride was effected in two stages by the successive addition of methanol and water. Mineral acid was omitted in order to preclude possible ring closure between a hydroxyl and the methallyl group. The diols II were converted to the crystalline dicarbamates III (Table II).

Tetrahydrofurans have been prepared by the acid-catalyzed ring closure of γ-unsaturated monoalcohols (1–3). When 2-substituted-2-methallyl-1,3-propanediols (II) were contacted with concentrated hydrochloric or sulphuric acid, the hitherto unreported cyclic 2,2-dimethyl-4-substituted-4-hydroxymethyltetrahydrofurans (IV) were obtained. This conversion occurred most satisfactorily when the diols II were treated with 1–3 volume per cent of concentrated hydrochloric acid in the presence of a solvent. Tetrahydrofuran was particularly suitable since the cyclization was readily controlled and the reaction mixture could be used directly in the preparation of carbamates. When methanol was used as a diluent, there was no indication that it supplanted or competed with the primary alcoholic function of II because IV was the sole product. This is an interesting finding in view of the mechanism of cyclization proposed below. The use of a larger amount of acid led to a decrease in the yield of IV. For example, with 2-allyl-2-

TABLE II

Substituted 1,3-propanediol dicarbamates

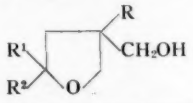


No.	R	R¹	% Yield	M.p., °C	Formula	Carbon %		Hydrogen %		Nitrogen %	
						Calcd.	Found	Calcd.	Found	Calcd.	Found
—	H	$CH_2CH{=}CH_2$	62.8	112.5–114°	$C_8H_{14}N_2O_4$	47.52	47.39	6.98	6.71	13.86	13.80
IIIa	H	$CH_2C(CH_3){=}CH_2$	54.5	161–163°	$C_9H_{16}N_2O_4$	50.00	50.59	7.46	7.54	12.96	13.11
IIIb	CH_3	$CH_2C(CH_3){=}CH_2$	67.0	155–156°	$C_{10}H_{18}N_2O_4$	52.15	51.80	7.88	7.48	12.17	12.25
IIIc	CH_2CH_3	$CH_2C(CH_3){=}CH_2$	65.9	161–163°	$C_{11}H_{20}N_2O_4$	54.07	53.74	8.25	8.18	11.47	11.59
IIId	$CH_2CH_2CH_3$	$CH_2C(CH_3){=}CH_2$	44.5	147–148°	$C_{12}H_{22}N_2O_4$	55.79	55.80	8.59	8.54	10.85	11.07
IIIe	$CH_2CH{=}CH_2$	$CH_2C(CH_3){=}CH_2$	43.8	130–131.5°	$C_{12}H_{20}N_2O_4$	56.22	56.29	7.87	7.80	10.93	11.00
IIIf	$CH_2C{\equiv}CH$	$CH_2C(CH_3){=}CH_2$	37.4	178–181°	$C_{12}H_{18}N_2O_4$	56.66	56.53	7.13	6.98	11.02	11.34
IIIg	C_6H_5	$CH_2C(CH_3){=}CH_2$	9.5	101.5–103°	$C_{15}H_{20}N_2O_4$	61.63	61.47	6.90	6.89	9.59	9.46

methallyl-1,3-propanediol (II*e*), not only did the expected cyclization occur, but also the allyl group and the remaining hydroxyl group tended to interact. Whereas methallyl-substituted diols underwent facile isomerization, 2-allyl-1,3-propanediol (XI) required prolonged treatment with a larger amount of acid. The cyclized products IV (Table III) were converted to the crystalline carbamates V (Table IV).

TABLE III

Substituted 4-hydroxymethyltetrahydrofurans



No.	R	R^1	R^2	% Yield	B.p. °C	B.p. mm
XII	H	CH_3	H	66.3	75–78°	5
IV*a*	H	CH_3	CH_3	65.0	—	—
IV*b*	CH_3	CH_3	CH_3	72.0	92–105°	15
IV*c*	CH_2CH_3	CH_3	CH_3	96.4	118–124°	15–20
IV*d*	$CH_2CH_2CH_3$	CH_3	CH_3	94.2	120–127°	15
IV*e*	$CH_2CH{=}CH_2$	CH_3	CH_3	91.9	122–126°	15
IV*f*	$CH_2C{\equiv}CH$	CH_3	CH_3	76.5	110–125°	8
IV*g*	C_6H_5	CH_3	CH_3	47.2	95–140°	0.1–0.2

The cyclization of 2-substituted-2-methallyl-1,3-propanediols (II) may be shown as occurring via an ionic mechanism (Fig. 2). Thus a proton adds to the olefin II to give a

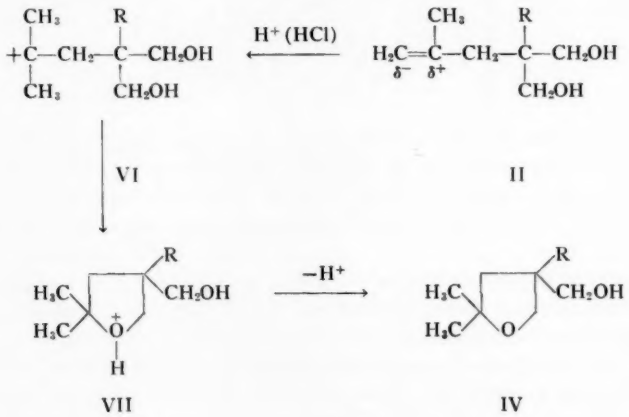
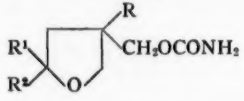


FIG. 2.

tertiary carbonium ion VI. Intramolecular reaction between the charged carbon atom of VI and one of the primary hydroxyl groups affords an oxonium ion VII from which a proton is expelled giving IV. Such a mechanism allows for the formation, via a Markownikoff addition, of a tetrahydrofuran rather than a tetrahydropyran ring and also depicts the catalytic role of hydrogen ion in promoting such a reaction.

TABLE IV

Substituted 4-carbamyloxymethyltetrahydrofurans



No.	R	R¹	R²	% Yield	M.p., °C	Formula	Carbon %		Hydrogen %		Nitrogen %	
							Calcd.	Found	Calcd.	Found	Calcd.	Found
—	H	CH_3	H	63.6	75–76.5°	$C_7H_{13}NO_3$	52.81	52.99	8.23	8.12	8.80	8.88
V*a*	H	CH_3	CH_3	41.5	99–101°	$C_8H_{15}NO_3$	55.47	55.51	8.73	8.56	8.09	8.19
V*b*	CH_3	CH_3	CH_3	83.1	46.5–47.5°	$C_9H_{17}NO_3$	57.75	57.79	9.16	9.08	7.48	7.36
V*c*	CH_3CH_2	CH_3	CH_3	74.5	53.5–54.0°	$C_{10}H_{19}NO_3$	59.66	59.63	9.51	9.50	6.96	7.17
V*d*	$CH_3CH_2CH_2$	CH_3	CH_3	57.7	59.0–59.5°	$C_{11}H_{21}NO_3$	61.36	61.28	9.83	9.44	6.51	6.56
V*e*	$CH_2CH{=}CH_2$	CH_3	CH_3	89.1	55–57°	$C_{11}H_{19}NO_3$	61.93	62.01	8.98	8.85	6.57	6.70
V*f*	$CH_2C{\equiv}CH$	CH_3	CH_3	66.2	88–92°	$C_{11}H_{17}NO_3$	62.54	62.48	8.11	7.89	6.63	7.06
V*g*	C_6H_5	CH_3	CH_3	34.9	85–86°	$C_{14}H_{19}NO_3$	67.43	67.52	7.68	7.24	5.62	5.53

Assignment of structure IV to the products of cyclization was supported by infrared absorption data. The isomerization of 2-substituted-2-methallyl-1,3-propanediols (II) to IV required an increase in the number of methyl groups from one to two, the appearance of a cyclic ether group, and the loss of the methallyl and a hydroxyl group. An inspection of the infrared spectra of II and IV showed that these changes did occur. They were exhibited by the appearance in the 7.25–7.35 μ region of a doublet (*gem*-dimethyl) in place of a single band (methyl), the loss of the 11.2 μ band (methallyl), the narrowing and shifting of the hydroxyl band from 3.0 to 2.95 μ, and finally the shifting of the 9.6–9.8 μ band (hydroxyl) to 9.5–9.6 μ (hydroxyl, cyclic ether) (6). In addition IV possessed a strong unassigned band at 12.95 μ.

Supporting evidence for the formulation of the cyclic compounds IV was obtained by cleaving the ring of IV*e*, a typical member of the group. Surprisingly, in this instance, the use of methods that have been described for the cleavage of tetrahydrofurans (7–11) led to intractable mixtures. However, the conversion was effected by applying a method used successfully in the field of sapogenin chemistry (12–14). Thus acetic anhydride – pyridine hydrochloride (12) readily converted IV*e* in excellent yield to 2-allyl-2-methallyl-1,3-propanediol diacetate (X), identical with a sample prepared by the acetylation of II*e* (Fig. 1). Hence, the methallyl and hydroxyl groups that had disappeared during the cyclization of the diol II to the isomeric IV, have reappeared upon ring opening.

Additional chemical evidence for the structures of 2,2-dimethyl-4-substituted-4-hydroxymethyltetrahydrofurans (IV) was obtained by the elimination of the hydroxyl group. Thus IV*b* was tosylated and the ester VIII*b* reduced with lithium aluminum hydride (15) to 2,2,4,4-tetramethyltetrahydrofuran (IX*b*) (Fig. 1). The infrared absorption curve and boiling point of IX*b* were the same as those previously reported (16). The 4-allyl analogue IV*e* was similarly converted to the expected 2,2,4-trimethyl-4-allyltetrahydrofuran (IX*e*) as judged by infrared analysis, where bands typical of the tosyl group appeared in the spectrum of VIII*e*, and disappeared in that of IX*e*. IV*e*, VIII*e*, and IX*e* exhibited bands denoting the presence of the allylic double bond, methyl groups, and the cyclic ether linkage.

2,2-Dimethyl-4-allyl-4-hydroxymethyltetrahydrofuran (IV*e*) was hydrogenated over platinum giving 2,2-dimethyl-4-*n*-propyl-4-hydroxymethyltetrahydrofuran (IV*d*). IV*d* was also obtained when diethyl *n*-propylmethallylmalonate (I*d*) was reduced with lithium aluminum hydride to 2-*n*-propyl-2-methallyl-1,3-propanediol (II*d*) and subsequently ring-closed with mineral acid.

The monocarbamates V were more active than the dicarbamates III upon the central nervous system of animals. The allyl derivative V*e* was particularly effective as an anticonvulsant (17). More comprehensive results of the pharmacological evaluation will be reported elsewhere.

EXPERIMENTAL

Boiling points and melting points (Fisher–Johns apparatus) are uncorrected. Infrared absorption spectra were obtained with a Beckman IR-5 spectrophotometer equipped with a sodium chloride prism. Solids were examined in potassium bromide pellets and liquids either as thin films or as solutions in carbon disulphide.

Preparation of Mono- and Di-substituted Malonates

Diethyl sodiomalonate and diethyl sodio-alkyl- (and -alkenyl-) malonates were treated

with the appropriate alkyl halide (bromide or chloride) in the customary manner giving the corresponding mono- and di-substituted malonates. These were purified by distillation *in vacuo*. The preparation of some of these malonates has been described (18). Diethyl methylmalonate (Sapon), diethyl ethylmalonate (Distillation Products Industries), diethyl *n*-propylmalonate (Sapon), and diethyl phenylmalonate (Benzol Products) were used without further purification.

Preparation of Substituted 1,3-Propanediols

The following procedure illustrates the general method used for preparing the 1,3-propanediols listed in Table I. A solution of 100 g of diethyl allylmethallylmalonate (I*e*) in 246 ml of anhydrous ethyl ether was added dropwise over a 3-hour period to a well-dispersed and vigorously stirred mixture of 22.5 g of lithium aluminum hydride in 554 ml of anhydrous ethyl ether maintained below 25° C in an atmosphere of nitrogen. The reaction mixture was stored overnight at room temperature. Excess hydride was discharged by the addition of 27.2 ml of methanol in 66 ml of ethyl ether; the resulting complexes were decomposed by the successive addition of 15.6 ml of 50% methanol and 31.2 ml of water while maintaining the temperature of the mixture below 25° C. The ethereal phase was separated and the residual solids were washed four times with ethyl ether. The combined ethereal extracts were washed with water twice, filtered, and evaporated, leaving 65.2 g (97.5%) of crude 2-allyl-2-methallyl-1,3-propanediol (II*e*). Infrared: λ_{max} 3.0 (hydroxyl), 3.25, 6.1 (unsaturation), 7.25 (methyl), 9.6–9.8 (hydroxyl), 10.9 (allyl), 11.25 (methallyl) μ. This product was distilled *in vacuo* and used directly for the preparation of either 2,2-dimethyl-4-allyl-4-hydroxymethyltetrahydrofuran (IV*e*) or 2-allyl-2-methallyl-1,3-propanediol dicarbamate (III*e*).

Cyclization of 2-Methallyl-1,3-propanediols (II)

The general procedure used for the cyclization of 2-methallyl-1,3-propanediol and 2-substituted-2-methallyl-1,3-propanediols to give the 2,2-dimethyl- and 2,2-dimethyl-4-substituted-4-hydroxymethyltetrahydrofurans, listed in Table III, is illustrated by the following example.

A solution of 65.2 g of 2-allyl-2-methallyl-1,3-propanediol (II*e*) in 40.5 ml of dry tetrahydrofuran was treated at room temperature with 1 ml of concentrated hydrochloric acid. The solution was warmed gently until, at approximately 50° C, an exothermic reaction occurred. External heating was discontinued while the temperature of the reaction mixture rose spontaneously to 94° C. The solution was then refluxed for 2 hours. The solvent was removed under reduced pressure and the residue distilled giving 59.9 g of 2,2-dimethyl-4-allyl-4-hydroxymethyltetrahydrofuran (IV*e*), b.p. 122–126° C/5 mm. The cyclization of II*e* was also effected with 0.5–1.0 volume per cent of hydrochloric acid in the absence of solvent. However, the reaction was extremely vigorous and difficult to control by external cooling. The yield of IV*e* was substantially decreased.

Cyclization of 2-Allyl-1,3-propanediol (XI)

2-Allyl-1,3-propanediol (XI) was cyclized by more drastic conditions than those described above. Thus a mixture of 11 g of XI and 1 ml of concentrated hydrochloric acid was refluxed for 17 hours. Following removal of the hydrochloric acid, distillation of the product (10.9 g) yielded 7.3 g (66.3%) of 2-methyl-4-hydroxymethyltetrahydrofuran (XII), b.p. 75–78° C/5 mm. The infrared spectrum possessed a strong band at 7.25 μ (C—CH_3) but no band indicative of a double bond.

Preparation of 2,2-Disubstituted 1,3-Propanediol Dicarbamates (III)

The procedure using tetrahydrofuran as solvent (19) was found to be superior to that wherein chloroform–toluene served as solvent and antipyrine was included as a hydrogen chloride acceptor (20). The products III (Table II) were recovered from the reaction mixtures by chilling the aqueous solutions after evaporating the organic solvent, and were recrystallized from aqueous alcohol. (Infrared: λ_{max} 2.95, 5.85, 6.2 μ (primary amide).)

Preparation of 2,2-Dimethyl-4-substituted-4-carbamyloxytetrahydrofurans (V)

The method used for preparing V (Table IV) was a modification of that applied above. The following example was typical of the procedure. A solution of 57.3 g of IV*e* in 77.6 ml of tetrahydrofuran was added dropwise during 1 hour to 55.2 g of phosgene dissolved in 63.1 ml of cold tetrahydrofuran (−8 to 4° C). The mixture was stirred for 30 minutes at this temperature and then stored overnight at room temperature. The solution was added over a 1-hour period to a stirred mixture of 276 ml of concentrated ammonium hydroxide and 3.4 g of sodium bisulphite maintained at 10–27° C (subsequent study showed that bisulphite could be omitted). After stirring for ½ hour, sufficient water was added to dissolve the solids. Distillation afforded a residue that was extracted four times with ether. The combined ethereal extracts were washed twice with 25-ml portions of water and the ether removed. The residue (72.6 g) was distilled giving 67.7 g of V*e*, b.p. 111–119° C/0.02–0.04 mm, solidifying at room temperature. The material was crystallized from ether – petroleum ether giving 64 g (89.1%) of V*e*, m.p. 55–57° C. When the distillation of crude material was omitted, V*e* was obtained in lower yield. The substance could also be crystallized from acetone – petroleum ether, aqueous methanol, or methanol – petroleum ether. Molecular weight (Rast): calc. 213; found 211, 216. Infrared: λ_{max} 3.0, 5.8, 6.2 (primary amide), 3.25, 6.1 (unsaturation), 10.95 (allyl), 7.25, 7.35 (*gem*-dimethyl), 12.95 μ.

Preparation of 2,2-Dimethyl-4-allyl-4-hydroxymethyltetrahydrofuran (IVe) from the Carbamate Ve

A mixture of 16 g of 2,2-dimethyl-4-allyl-4-carbamyloxymethyltetrahydrofuran (V*e*) (m.p. 54.0–55.5° C), 12 g of sodium hydroxide, and 250 ml of ethanol was refluxed for 8 hours. After dilution with water, the ethanol was removed by distilling *in vacuo*. The aqueous residue was cooled, saturated with sodium chloride, and extracted five times with ethyl ether. The ethereal extracts were washed with water and reduced to dryness. The resulting oily product was vacuum-distilled, yielding 8.2 g (64%) of IV*e*, b.p. 116–117° C/10–15 mm. Analysis: Calc. for $C_{10}H_{18}O_2$: C, 70.56; H, 10.66. Found: C, 70.17; H, 10.45. Main infrared absorption bands: λ_{max} 2.95, 3.25, 3.40, 3.50, 6.10, 6.90, 7.08, 7.23, 7.78, 8.24, 8.40, 8.56, 8.90, 9.4–9.75, 10.05, 10.95, 11.42, 11.60, 12.94 μ.

Preparation of 2-Allyl-2-methallyl-1,3-propanediol Diacetate (Xe)

(a) From 2-Allyl-2-methallyl-1,3-propanediol (IIe) by Acetylation

A solution of 20 g of 2-allyl-2-methallyl-1,3-propanediol (II*e*) in 110 ml of acetic anhydride and 22 ml of anhydrous pyridine was heated for 1 hour on a steam bath and then allowed to stand for 18 hours at room temperature. The solution was poured into 400 ml of cold water and the mixture stirred for 1 hour at room temperature. The mixture was extracted five times with ethyl ether and the combined ethereal extracts washed successively with water, 5% hydrochloric acid, saturated saline solution, 5% sodium bicarbonate, and finally with water. After drying over sodium sulphate, the solvent was

removed leaving 28.42 g (95%) of the crude acetate. Distillation of this product afforded 2-allyl-2-methallyl-1,3-propanediol diacetate (X*e*), b.p. 153–157° C/16 mm, λ_{max} 5.78, 8.0–8.2, 9.6–9.7 (ester), 3.25, 6.1, 10.9–11.2 (unsaturation) μ.

(b) From 2,2-Dimethyl-4-allyl-4-hydroxymethyltetrahydrofuran (IVe) by Treatment with Acetic Anhydride – Pyridine Hydrochloride

A stream of hydrogen chloride was passed into a mixture of 150 ml of acetic anhydride and 12 ml of pyridine until 5.2 g had been absorbed. After adding 22.86 g of 2,2-dimethyl-4-allyl-4-hydroxymethyltetrahydrofuran (IV*e*) the solution was refluxed for 5 hours and then stored overnight at 5° C. Excess anhydride was decomposed by adding 2000 ml of water and stirring the mixture for 1 hour. The mixture was worked up as described in procedure (*a*) to give 33.8 g (98.9%) of crude product. Several distillations of this material gave X*e*, b.p. 155–160° C/17 mm. The infrared spectrum was identical with that of the product from procedure (*a*).

Catalytic Reduction of 2,2-Dimethyl-4-allyl-4-hydroxymethyltetrahydrofuran (IVe)

A solution of 23.53 g of 2,2-dimethyl-4-allyl-4-hydroxymethyltetrahydrofuran (IV*e*) in 300 ml of ethanol was shaken with hydrogen and 0.5 g of platinum oxide under slightly positive pressure. Approximately 1 mole of hydrogen was absorbed within 30 minutes. Following removal of the catalyst, the solvent was evaporated giving 23.6 g of a yellow oil. Distillation *in vacuo* afforded 20.6 g (87.4%) of 2,2-dimethyl-4-*n*-propyl-4-hydroxymethyltetrahydrofuran (IV*d*) as a colorless oil, b.p. 50–65° C/0.06–0.07 mm. The infrared spectrum of IV*d* indicated the absence of unsaturation and was indistinguishable from that of a sample prepared from diethyl *n*-propylmethallylmalonate (I*d*) by reduction and subsequent ring closure.

Conversion of 2,2,4-Trimethyl-4-hydroxymethyltetrahydrofuran (IVb) to 2,2,4,4-Tetramethyltetrahydrofuran (IXb)

(a) 2,2,4-Trimethyl-4-tosyloxymethyltetrahydrofuran (VIIIb)

p-Toluenesulphonyl chloride (79 g) dissolved in 140 ml of redistilled pyridine was added during 1 hour to a vigorously stirred solution of 39.3 g of 2,2,4-trimethyl-4-hydroxymethyltetrahydrofuran (IV*b*) in 140 ml of redistilled pyridine, maintained at 5° C. The mixture was stirred with cooling for an additional 3 hours and left overnight at room temperature. It was poured onto crushed ice and acidified with concentrated hydrochloric acid. The mixture was extracted six times with ethyl ether, and the combined ethereal extracts washed to neutrality with water and evaporated, affording 79.5 g (97.7%) of crude tosylate VIII*b*. The substance was not purified but used directly for the following reduction. Infrared: λ_{max} 6.25, 7.3–7.4, 8.4–8.5, 10.3–10.5, 10.95, 11.3, 12.7, 14.2, 15.0 μ (aromatic, tosyl).

(b) Lithium Aluminum Hydride Reduction of 2,2,4-Trimethyl-4-tosyloxymethyltetrahydrofuran (VIIIb)

A solution of 79.5 g of tosylate VIII*b* in 400 ml of anhydrous ethyl ether was added dropwise during 1 hour at 25–30° C to 16.2 g of lithium aluminum hydride dissolved in 800 ml of anhydrous ethyl ether. The mixture was refluxed for 8 hours with vigorous stirring, cooled, and decomposed with ice and water. The solids were repeatedly extracted with ethyl ether, and the combined ethereal extracts washed with water and concentrated, yielding 27.8 g of yellow oil. Two distillations of this oil gave 12.9 g of 2,2,4,4-tetramethyltetrahydrofuran (IX*b*) boiling at 116–118° C, n_D^{20} 1.422; reported (16) boiling

point 120° C and n_D^{20} 1.4061. The infrared spectrum of IX*b* was identical with that reported (16).

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RADIATION-INDUCED EXCHANGE REACTIONS IN SOLUTIONS OF HYDROGEN IN WATER[1]

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ABSTRACT

The exchange of H, D, and T atoms between water and dissolved hydrogen has been studied in both heavy and light water solutions. Values of the "exchange yield", G_{tracer}, for the isotopic hydrogen atoms have been deduced and are identified with the yield of D atoms from HDO in H_2O, H atoms from HDO in D_2O, T atoms from HTO in H_2O and from DTO in D_2O. These values are correlated by assuming that the medium, H_2O or D_2O, affects the total probability of dissociation of the tracer molecule (HDO, HTO, DTO) and that in HDO H atoms are more readily dissociated than D atoms.

INTRODUCTION

The radiation-induced exchange of hydrogen atoms (H, D, or T) between water and dissolved hydrogen is a direct observation of the presence and reaction of these atoms and provides a further method of studying the difference in radiolytic yields between heavy and light water.

This exchange was first studied by Gordon and Hart (1), who irradiated a solution of D_2 in H_2O with Co^{60} γ rays and found that HD and H_2 appeared in the dissolved gas. The initial yield of HD in neutral solution was found to be about 2.7 molecules/100 ev, equal to the yield of hydrogen atoms in pure water. They advanced the mechanism:

$$H_2O \rightsquigarrow H + OH \quad [1]$$

$$H_2O \rightsquigarrow \tfrac{1}{2}H_2 + \tfrac{1}{2}H_2O_2 \quad [2]$$

$$H + D_2 \rightarrow HD + D \quad [3]$$

$$OH + D_2 \rightarrow HOD + D \quad [4]$$

$$D + D \rightarrow D_2 \quad [5]$$

In this scheme every hydrogen atom produced in reaction [1] is detected by exchange in reaction [3]. Hydrogen is produced with the "molecular" yield, $G \simeq 0.4$ by reaction [2], but the total amount of dissolved hydrogen ($H_2 + HD + D_2$) remains constant.

If the dissolved hydrogen is a mixture of isotopic species, H_2 and D_2 say, then reaction [3] may be followed by

$$D + H_2 \rightarrow HD + H \quad [6]$$

and this H atom may react again by reaction [3]. A chain reaction is now observable in which the yield of HD is about 60, much greater than the initial yield of H atoms. Chain reactions in this system have been studied in detail by Friedman and Zeltman (2) whose results were in agreement with Gordon and Hart where comparison was possible.

Bardwell and Dyne (3) followed the initial exchange reaction (3) by a tracer technique. Hydrogen gas was dissolved in H_2O containing about 1% HDO. The only exchanges observed are those in which an HDO molecule is dissociated and gives a D atom; on a statistical basis these amount to $\sim 1/200$ of the total number of initial exchanges (reactions [1] and [3] in the above scheme). The results were calculated on the assumption

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that there was no isotopic discrimination in the production or reaction of the tracer D atoms; the initial "total exchange" yield was found to be much less than the primary yield of H atoms in H_2O.

In a subsequent paper (5) it was suggested that an excited HDO molecule dissociated less frequently to give D atoms than H atoms. The "total exchange" yield calculated from data obtained with D atoms as tracers would therefore be less than the hydrogen atom yield in pure water. This paper describes further tracer experiments using H and T atoms in which the interest centers on the differing availability of H, D, and T atoms from the mixed molecules, HTO, HDO, and DTO.

EXPERIMENTAL

The technique used for isolating gases dissolved in water was that described by Bardwell and Dyne (3). In this method one sample of water is used for several determinations. A check on the consistency of these experiments is obtained when different samples of water, with different concentrations of tracer atoms, give compatible results, when plotted as in Figs. 1 and 2. Reproducible results, comparable with those obtained in other laboratories, were obtained when the following method was used: water was purified by distillation, followed by distillation from alkaline permanganate followed by distillation in a stream of oxygen, the mixture of steam and oxygen being passed through a quartz tube heated to 700° C. In a private communication E. J. Hart tells us that small amounts of peroxide may be formed above 700° C. The water was degassed by freezing with solid CO_2, pumping, and thawing several times using a vacuum system

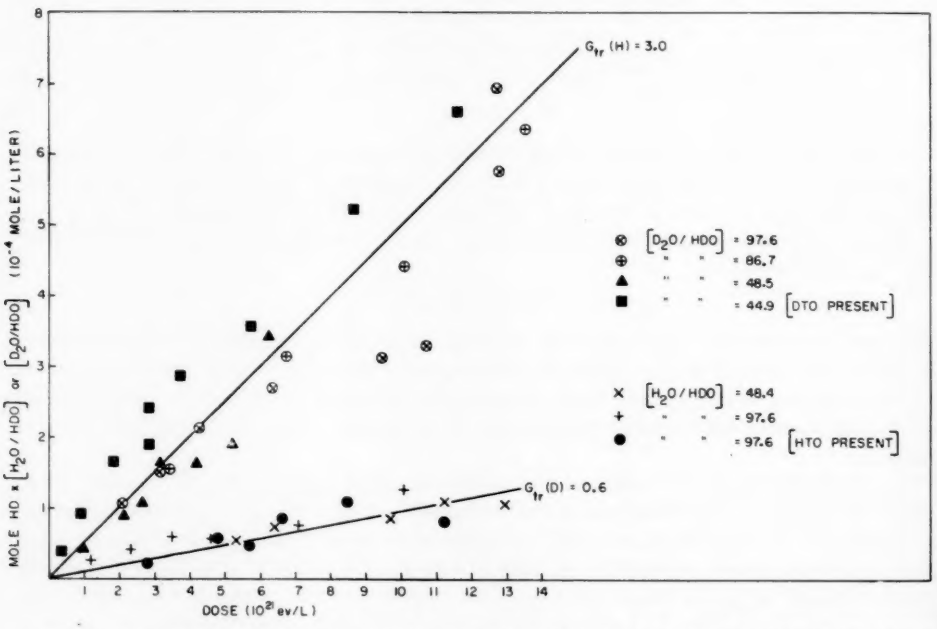
MOLE HD x [H2O/HDO] or [D2O/HDO] (10⁻⁴ MOLE/LITER)
DOSE (10²¹ ev/L)
Gir (H) = 3.0
Gir (D) = 0.6
[D2O/HDO] = 97.6
" " = 86.7
" " = 48.5
" " = 44.9 [DTO PRESENT]
[H2O/HDO] = 48.4
" " = 97.6
" " = 97.6 [HTO PRESENT]

FIG. 1. Formation of HD in tracer experiments on the radiolysis of solutions of H_2 in H_2O and D_2 in D_2O. The upper line is for experiments using H atoms as a tracer in D_2O, the lower line is for D atoms as a tracer in H_2O.

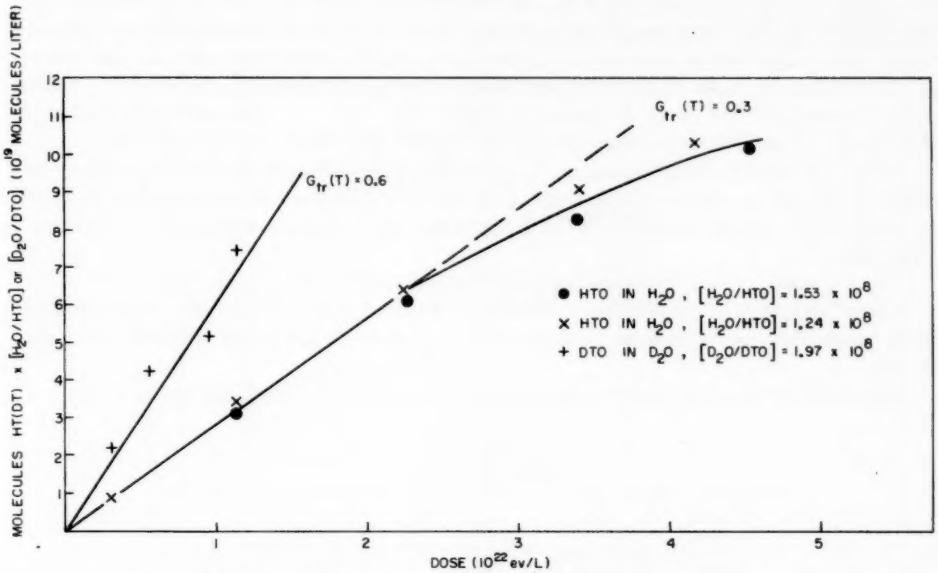
MOLECULES HT(DT) × [H2O/HTO] or [D2O/DTO] (10^9 MOLECULES/LITER)
DOSE (10^22 ev/L)
G_fr (T) = 0.6
G_fr (T) = 0.3
● HTO IN H2O , [H2O/HTO] = 1.53 × 10^8
× HTO IN H2O , [H2O/HTO] = 1.24 × 10^8
+ DTO IN D2O , [D2O/DTO] = 1.97 × 10^8

FIG. 2. Exchange of tritium atoms between water, H_2O or D_2O, containing tritium with dissolved hydrogen or deuterium.

with stopcock joints lubricated by Kel-F grease. The sample of water was saturated with H_2 or D_2 which had been passed into the system through a charcoal trap cooled with liquid air, and the saturated solution irradiated overnight. The dissolved hydrogen was pumped away and the cell was then filled with H_2 or D_2 for the first run. Without this preirradiation, low yields were invariably obtained.

Tritiated water with a specific activity of 4.5 mc/g was diluted to give solutions containing in the order of ~10 μcuries T/ml and was purified by distillation as described above. The absolute tritium content was determined by gas-counting a sample of electrolyzed water (10). In the exchange experiments the whole sample of dissolved gas was pumped into the counter. Total counting rates were in the range 100–1000 c.p.m. in a system which detected $\frac{1}{3}$ of the total disintegrations. Corrections were made for the tritium content of the D_2 and D_2O used.

Mass spectrometric analysis for HD, H_2, and D_2 was carried out on a Consolidated 21-610 instrument. The analytical precision at a concentration of 0.5% HD in D_2 is about 10% and improves as the concentration increases.

Irradiations were carried out in the Co^{60} source described previously (3). The dose rate, $\sim 1 \times 10^{22}$ ev/l./hr, was determined by the Fricke dosimeter taking $G(Fe^{3+}) = 15.5$ ions/100 ev.

EXPERIMENTAL RESULTS

Results of tracer experiments are expressed as "total exchanges": the number of exchanges observed (number of atoms T appearing in dissolved gas per liter of solution or the number of HD molecules formed per liter of solution) multiplied by the ratio of unlabelled molecules to labelled molecules e.g. H_2O/HDO, D_2O/HDO, H_2O/HTO,

D_2O/DTO as the case may be. For experiments with H or D as a tracer this ratio is between 40 to 100, for experiments with tritium it is of the order of 1.5×10^8. We call the G values obtained in this way G(tracer) or G_{tr}. G_{tr}(D) from HDO may be thought of as the yield of D atoms from HDO per 100 ev absorbed in the HDO molecule. In terms of the "reactivity" of H or D atoms, values of G_{tr} must be compared with $\frac{1}{2}G$(H) in H_2O or $\frac{1}{2}G$(D) in D_2O since these molecules contain two labile atoms/molecule.

As will be seen in the discussion, G_{tr} is a quantity determined both by the tracer atom, H, D, or T, and by the solvent. For rigorous definition we refer to G_{tr}(H, D_2O) or G_{tr}(T, H_2O) giving both the tracer atom and the solvent in which the exchange is observed.

In the discussion we estimate values of G_{tr}(H, H_2O) and G_{tr}(D, D_2O), the "total exchange" yields of H atoms from HDO in H_2O, and of D atoms from HDO in D_2O; these quantities are, of course, unobservable but have considerable theoretical significance.

Values of G(tr) determined from the slopes of lines in Figs. 1 and 2 are given in Table I.

TABLE I

Values of G(tracer)

Tracer molecule	Solvent	Solute	G(tr)
HDO	D_2O	D_2	$G_{tr}(H,D_2O) = 3.0\pm0.5$
HDO	H_2O	H_2	$G_{tr}(D,H_2O) = 0.6\pm0.1$
HTO	H_2O	H_2	$G_{tr}(T,H_2O) = 0.3\pm0.05$
DTO	D_2O	D_2	$G_{tr}(T,D_2O) = 0.6\pm0.1$

The limits of error are arbitrarily determined from the scatter of the points and the slopes of the most extreme lines that could reasonably be drawn through them. The experimental points for G_{tr}(H, D_2O) show the largest scatter and it is also noteworthy that some of the initial points lie on a line of significantly greater slope. (G(tr) = 5.0 or more.) In series of results in which this was observed, such as those with (D_2O/HDO) = 44.9, the points for greater doses lay on a line parallel to that drawn in the figure. We have no explanation of this but conclude that G_{tr}(H, D_2O) = 3.0 can be taken as a minimum value.

The value of G_{tr}(D, H_2O) agrees well with that obtained by Bardwell and Dyne (3). It should be noted that their "exchange yield" is twice G(tr) as defined here; consequently their exchange yield of 1.0 is equivalent to G_{tr}(D, H_2O) = 0.5.

Experiments in which D_2 was dissolved in pure H_2O and H_2 dissolved in pure D_2O were also carried out. These experiments are of course not "tracer" experiments, since every exchange is observed. The results are given in Table II. The first series of experiments is simply a repetition of Gordon and Hart's original experiment, and the results are in good agreement with their results. The value of G(HD) from D_2O is the first determination of this quantity in neutral solution.

TABLE II

Values of G(HD) in H_2O and D_2O

Solvent	Solute	G(HD)	$\frac{1}{2}G$ ($\equiv G_{tr}$)
H_2O	D_2	2.9±0.1	1.45
D_2O	H_2	3.7±0.1	1.85

A small pressure dependence was observed in these experiments. Yields measured at small doses (1×10^{21} ev/l.) are shown in Fig. 3. This is negligible in the range of dissolved

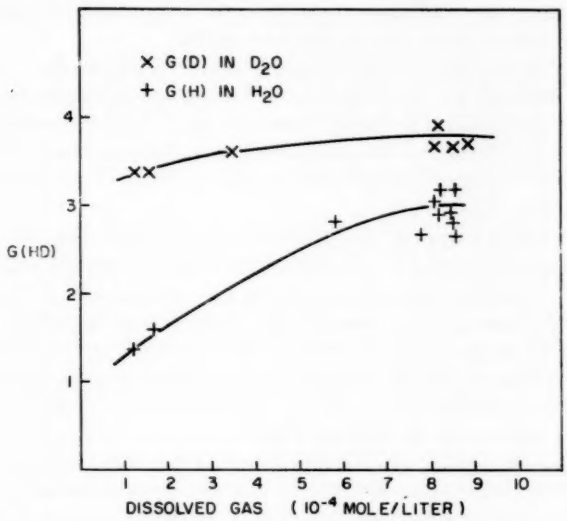

FIG. 3. Variation of G(HD) with partial pressure of dissolved D_2 in H_2O or dissolved H_2 in D_2O. Doses of $\sim1\times10^{21}$ ev/l. were given for all the data presented.

gas concentrations of $5\text{–}10\times10^{-4}$ mole/liter but is appreciable at lower concentrations. In this matter our data are not in serious disagreement with other workers who were working in the higher-pressure ranges.

In agreement with Gordon and Hart, yields of H_2 in H_2O solutions and D_2 in D_2O solutions were also observed which are identified with the molecular process, reaction [2]. Values of $G(H_2)$ lay in the range 0.4–0.5, and values of $G(D_2)$ in the range 0.3–0.35. $G(H_2)$ increased as the pressure of dissolved deuterium decreased.

DISCUSSION

In comparing values of G_{tr}, G(H), and G(D) two effects must be distinguished: there are effects of the medium (H_2O or D_2O) on the effective probability of dissociation of the tracer molecule, and effects due to the differing detachment probabilities of, for instance, H and D atoms from an excited HDO molecule.

The first effect, the influence of the properties of the medium on the initial radiolytic steps, is possibly the origin of the isotope effects in the primary yields in heavy and light water. These isotope effects have been discussed by many workers (4, 5, 7, and 8): the current conclusions are firstly that differences in the rate constants and diffusion constants between H and D atoms and between OH and OD radicals will not affect the product yields. Secondly, Armstrong, Collinson, and Dainton (4) suggest that a more extended initial distribution of D atoms in spurs in D_2O, relative to the initial distribution of H atoms in H_2O, would give the observed isotope effect, viz. $G(D_2) < G(H_2)$ and $G(D) > G(H)$; in the more extended, dilute distribution the probability of atom recombination to give molecular products is smaller and the probability of escape and reaction with the solute is greater. These workers suggested that the distribution of H or D atoms

was, at least in part, determined by rate of thermalization of the ~100-ev electrons formed in the initial ionization and by the time required for capture by the solvent molecules to form H_2O^- ions (which subsequently dissociate to give H and OH^-). The rates of these processes are intimately connected with the dielectric properties of H_2O and D_2O and may differ appreciably in the two media.

It follows from this suggestion that hydrogen atoms produced from the dissociation of HDO in a D_2O medium will be formed in a distribution characteristic of D_2O. They will have a greater probability of escape from the spur and of reacting with a solute than D atoms produced from the same molecule in a H_2O medium. Calculations have shown that there are no isotopic separations resulting from the reactions of H and D atoms in the same spur (5).

The magnitude of this effect of the medium can be estimated from the values of $G(D)$ and $G(H)$ (given in Table II). In neutral solution the present measurements give $G(D)/G(H) = 1.27$. In acid solution lower values, 1.11 (8) and 1.08 (9) are reported. We conclude that, in the absence of any isotopic discrimination in the detachment of H and D atoms from an HDO molecule, $G_{tr}(H, D_2O)$ would be 10–30% greater than $G_{tr}(D, H_2O)$.

The differing detachment probabilities of H and D atoms from an excited molecule can only be discussed qualitatively and by inference from mass-spectral studies on partially deuterated hydrocarbons. Isotope effects in mass spectra are fully summarized by Field and Franklin (6); the general conclusions are that in a partially deuterated hydrocarbon, detachment of H atoms is more probable than the detachment of D atoms, that detachment of an H atom in a partially deuterated molecule is more probable than the detachment of an H atom in the fully protonated molecule and, lastly, that there are no large changes in the total yields of molecular ions and fragments on isotopic substitution. We postulate that these conclusions are applicable to HDO.

To correlate our experimental results with these ideas, we have to eliminate the effect of the medium, i.e. $G_{tr}(D, H_2O)$ is to be compared with the "unobservable" quantity $G_{tr}(H, H_2O)$. Using our experimental ratio of $G(D)/G(H) = 1.27$ we put $G_{tr}(H, H_2O) = 1/1.27\, G_{tr}(H, D_2O)$. Similarly we correlate results in heavy water by comparing $G_{tr}(H, D_2O)$ with $G_{tr}(D, D_2O) = 1.27\, G_{tr}(D, H_2O)$.

With these corrections the ratio $G_{tr}(D)/G_{tr}(H)$ should be the same in H_2O and D_2O since it expresses a molecular property of HDO and not a property of the medium. The data should also be consistent with our expectation that there are no large isotope effects in the *total* probability of dissociation to give, for instance H and D atoms from HDO or to give two H atoms from H_2O. The approximate equalities $G_{tr}(H, H_2O)+G_{tr}(D, H_2O) \simeq G(H)$, and $G_{tr}(H, D_2O)+G_{tr}(D, D_2O) \simeq G(D)$ should be observed.

Values of $G_{tr}(H, H_2O)$ and $G_{tr}(D, D_2O)$ calculated using our ratio of $G(H)/G(D) = 1.27$ are given in brackets in Table III together with values of the sums and ratios referred to above.

The values of the sums agree well with the values of $G(H)$ and $G(D)$.

While the value of the ratio $G_{tr}(D)/G_{tr}(H)$ is, indeed, independent of the solvent this agreement is probably fortuitous. The limits of error on the ratio are large if upper and lower limiting values of G_{tr} are combined in this ratio; in D_2O for instance the values are 0.25 (+0.12, −0.07). It can only be claimed that the data are consistent with the postulate that the discrimination is analogous to "mass-spectral" isotope effects. The ratio $G_{tr}(D)/G_{tr}(H)$ is, in our interpretation, equivalent to the π factor (probability of dissociation of a D atom from HDO/probability of dissociation of an

TABLE III

Correlations of G(tracer)

	Medium	
	H_2O	D_2O
$G_{tr}(H)$	$(2.3_6 \pm 0.5)$	3.0 ± 0.5
$G_{tr}(D)$	0.6 ± 0.1	$(0.7_6 \pm 0.1)$
$G_{tr}(H) + G_{tr}(D)$	$2.9_6 \pm 0.6$	$3.7_6 \pm 0.6$
$G(H)$ or $G(D)$	2.9 ± 0.1	3.7 ± 0.1
$G_{tr}(D)/G_{tr}(H)$	0.25	0.25

H atom from HDO) for the mass spectrum of HDO. The mass spectrum of HDO is unknown but values of the π factor of 0.3–0.5 are observed in light hydrocarbons (6).

The experimental values of $G_{tr}(T)$ are also, in a more limited sense, consistent with the same postulate. No detailed comparison is possible without values of $G(T)$ in pure T_2O. In H_2O solutions one would expect T atoms to be less labile than D atoms in HDO and so $G_{tr}(T) < G_{tr}(D)$, as observed; in D_2O solutions again H from HDO would be much more labile than T in DTO and $G_{tr}(H) > G_{tr}(T)$ as observed.

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THE MECHANISM OF THE ALCOHOLYSIS OF ALIPHATIC NITRITES

I. ALCOHOLYSIS OF 1-METHYLHEPTYL NITRITE IN ALKALINE AND NEUTRAL SOLUTION[1]

A. D. ALLEN[2] AND G. R. SCHONBAUM[3]

ABSTRACT

A polarimetric study of the kinetics of the alcoholysis of 1-methylheptyl nitrite in alkaline solution has shown that the reaction rate is proportional to both the nitrite and alkoxide ion concentration. The asymmetric carbon center is not involved in the reaction. In strictly neutral solution no reaction occurs; the commonly observed "neutral" reaction is attributed to traces of acid formed in the decomposition of the nitrite ester. The mechanism of the reactions is discussed.

In a previous paper (1) the mechanism of the acid- and base-catalyzed hydrolysis of some organic nitrite esters was discussed, and some preliminary work on alcoholysis reported. With perchloric acid as the catalyst the rapid reaction was first order with respect to both the nitrite and acid concentrations, but with hydrochloric acid or added halide salts an additional catalysis, proportional to the halide ion concentration, was observed. In alkaline solution the much slower reaction was approximately first order with respect to both the nitrite and hydroxide ion concentration, but the second-order rate coefficient decreased slightly with increasing hydroxide concentration. Since this decrease was not a simple salt effect it indicated the possibility of a solvolytic reaction between the nitrite and water. It had been reported earlier that nitrite esters react readily with methanol, in the absence of added catalysts, evolving gaseous methyl nitrite (2). These observations prompted the present investigation into the uncatalyzed alcoholysis reaction. The indications, from our work using aqueous media, were that the solvolytic reaction would be too slow to account for the apparently rapid reaction with methanol.

The reversible reaction between an aliphatic nitrite and an alcohol may be written:

$$RONO + R'OH \rightleftarrows R'ONO + ROH \qquad R, R' = \text{alkyl.}$$

Some physical method must be used to follow the course of such a reaction, and the polarimetric method was chosen as the most suitable one. From our previous work (1) it was known that the specific rotation of (+)- or (−)-1-methylheptyl nitrite is just over half that of its hydrolysis product (+)- or (−)-octan-2-ol, and it seemed likely that, under the conditions to be used, complete retention of configuration would be observed. Preliminary experiments confirmed the following relationships, which had to be known precisely before any rate measurements could be made: (*a*) the optical rotations of solutions of the alcohol and nitrite are proportional to their concentrations, (*b*) the total rotation of mixtures of the two optically active compounds in solution is given by the sum of their individual rotations, and (*c*) the asymmetric center is not involved in the reactions to be studied, so that the optical configurations are preserved. During repeated esterification, hydrolysis, and alcoholysis in a wide variety of acidic and basic solutions, the optical purity of the alcohol recovered was always unchanged, confirming exclusive fission of the nitrosyl-oxygen bond. The rotations of these compounds in various solvents are given in Table I.

[1]*Manuscript received November 18, 1960.*
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TABLE I

Optical rotations of 10% (by weight) solutions at 25°

Solvent	(+)-Octan-2-ol α_D^{25} (l = 2)	(+)-1-Methylheptyl nitrite α_D^{25} (l = 2)
1-Propanol	1.58	0.59
1-Pentanol	1.65	0.60
2-Propanol	1.46	—
2-Methyl-2-butanol	1.45	0.56
Dioxane	2.27	—
Nitromethane	—	0.11

It is of interest to note that, whereas the rotation of 1-methylheptyl nitrite in alcoholic solution is relatively insensitive to the alcohol used, it is smaller by a factor of about five in nitromethane solution; also the rotation of octan-2-ol in dioxane is significantly higher than in alcoholic solution.

Equilibrium Measurements

The position of equilibrium for the over-all reaction

$$R^*ONO + R'OH \overset{H^+}{\rightleftharpoons} R^*OH + R'ONO$$

where $R^* = (+)$- or $(-)$-1-methylheptyl, $R' =$ alkyl, was determined. The measurements were carried out in acid solution to reduce the time needed to reach equilibrium, and it was shown that the concentration and the nature of the acid present had no effect on the final result. Values obtained for the concentration equilibrium constant $K_c = [R^*OH][R'ONO]/[R^*ONO][R'OH]$ at 25° were as follows.

R'OH	K_c
2-Methyl-2-butanol	0.28
2-Propanol	0.51
1-Propanol	1.6 (In dioxane)

With the tertiary and secondary alcohols the equilibrium position could be determined from simple mixtures of the alcohols and nitrite, but with the primary alcohol the reaction was displaced too far to the right for accurate measurement. Dioxane was used as a solvent to reduce the concentration of the alcohol. These results show that the equilibrium is shifted towards the products as the reagent is changed from tertiary, through secondary, to primary alcohol. Two mutually supporting effects would account for this trend, (*a*) the reactivity of nitrites in acid solution decreases in the order tertiary > secondary > primary, and (*b*) the nucleophilic strength of the alcohols decreases in the order primary > secondary > tertiary (11).

Kinetics and Mechanism of Alcoholysis in Alkaline Solution

The alcoholysis of 1-methylheptyl nitrite in alkaline solution was studied using 1-propanol as the solvent, in the presence of small concentrations of sodium propoxide. It was found that secondary and tertiary alcohols and alkoxides could not be used as reagents, for the following reason. The reversible reaction in alkaline solutions

$$R^*ONO + R'O^- \overset{\text{slow}}{\rightleftharpoons} R^*O^- + R'ONO \qquad (a)$$

is complicated by the further equilibrium

$$R^*O^- + R'OH \overset{\text{fast}}{\rightleftharpoons} R^*OH + R'O^-. \qquad (b)$$

If reaction (*b*) is displaced strongly towards the right the reagent alkoxide will be quantitatively regenerated and its concentration will remain constant throughout the reaction. Thus, if the reaction rate is given by $v = k_2$ [R*ONO][R′O$^-$], (as in alkaline hydrolysis) the kinetics observed would be pseudo first order, the rate coefficient being proportional to the (constant) concentration of alkoxide. Alternatively, if reaction (*b*) is displaced strongly towards the left, the reagent alkoxide would be consumed and second-order kinetics could, in principle, be observed. However, since in our experiments the nitrite is in very large excess over the alkoxide, the reaction would cease after a small fraction of the ester had reacted. Finally, if reaction (*b*) has an intermediate equilibrium position it will be difficult to determine with sufficient accuracy the concentrations of the two alkoxides at any point in the reaction and the kinetic order will be obscured. Displacement of equilibrium (*b*) to the left or right will depend on the relative basicities of the two alkoxides. The following order of decreasing basicity has been given (3): tertiary > secondary > primary alkoxide > hydroxide. The position of hydroxide at the lower end of this sequence presents a further problem, since, if there is any water present in the reaction mixture some hydroxide ion will be formed, which will give rise to the irreversible hydrolysis reaction

$$R^*ONO + HO^- \rightarrow R^*OH + NO_2^-.$$

Conversion of alkoxide to hydroxide, followed by production of nitrite ion, would again lead to early termination of the reaction. Extreme precautions were therefore necessary to ensure that all the solutions used were perfectly dry.

The alkoxide of octan-2-ol formed in the reaction is secondary, and it follows from the above that clear kinetic results could only be expected if the reagent were a much more weakly basic primary alkoxide. We should then expect to observe pseudo first-order kinetics. The results obtained are shown in Table II. Good first-order kinetics were

TABLE II

Reaction of 1-methylheptyl nitrite with sodium propoxide in 1-propanol at 25° C

$[R^*ONO]_0$ (M)	$[PrO^-]_0$ (10^2 M)	10^4 k_1 (sec^{-1})	$k_2 = \frac{k_1}{[PrO^-]}$
0.826	1.07	0.091	8.5
0.744	2.14	0.221	10.3
0.772	2.60	0.253	9.7
0.596	4.34	0.432	9.9
0.827	5.24	0.509	9.7

observed, the first-order rate coefficient (k_1) being satisfactorily proportional to the concentration of alkoxide. Several conclusions may be drawn from these results: (*a*) propoxide must be much less basic than octan-2-oxide, (*b*) the solutions were satisfactorily dry, (*c*) any contribution to the total reaction rate by reaction of the nitrite with the solvent alcohol is negligible, since otherwise the second-order rate coefficients would decrease with increasing alkoxide concentration. From this it follows that the alcoholysis reaction in neutral solution should be immeasurably slow, unless some other mechanism is possible which is inhibited by alkali.

Since the alkaline reaction proceeds without disturbing the asymmetric center, we envisage a bimolecular nucleophilic attack by alkoxide on the nitrogen atom of the ester molecule:

$$R'O^- + R^*ONO \underset{\text{fast}}{\overset{\text{slow}}{\rightleftharpoons}} \left[R^*O \cdots \overset{\overset{O}{\|}}{N} \cdots OR' \right]^- \underset{\text{slow}}{\overset{\text{fast}}{\rightleftharpoons}} R'ONO + R^*O^-,$$

followed by

$$R^*O^- + R'OH \xrightarrow{\text{fast}} R^*OH + R'O^-.$$

Alcoholysis Reactions in Neutral Solution

At the beginning of this investigation many kinetic runs were attempted using (+)- or (−)-1-methylheptyl nitrite prepared and purified in the usual way, with various alcohols and solvents similarly purified and dried. Reaction always occurred as soon as the reagents were mixed, but the rates of these reactions were quite random and could not be reproduced. Improvements in experimental technique, e.g. complete exclusion of oxygen, moisture, light, and nitrite decomposition products, gradually reduced the speed of the spontaneous reactions until, under optimum conditions, no reaction occurred on mixing the reagents. Generally a variable induction period of up to 48 hours was observed: reaction then started and in some cases it was possible to follow it kinetically. The results are given in Table III. The initial rates of these spontaneous reactions did not

TABLE III

Solvolysis of 1-methylheptyl nitrite at 25° C

$[R^*ONO]_0$ (M)	Solvent	Induction period (hr)	Approx. initial rate $10^4\ k_1$ (sec^{-1})
0.635	1-Propanol	—	0.35
0.564	"	48	0.35
0.503	"	—	0.55
0.360	2-Methyl-2-butanol	3	0.12
0.421	"	15	0.15
0.856	"	3	0.12
0.590	"	—	0.14
0.530	"	24 days	—*
0.447	85 Dioxane:7 propanol	18	—
0.488	70 Dioxane:15 nitromethane:7 propanol	3	—
0.466	35 Dioxane:50 nitromethane:7 propanol	2	1.2
0.461	25 Dioxane:60 nitromethane:7 propanol	—	4.0
0.455	5 Dioxane:80 nitromethane:7 propanol	—	Very fast

*In presence of 10^{-4} M sodium alkoxide.

depend on the length of the induction period, but were generally faster in 1-propanol than in 2-methyl-2-butanol. Induction periods were more usually observed in the tertiary than in the primary alcohol. Addition of traces (10^{-4} M) of alkali prolonged the induction period greatly. The use of mixed solvents containing varying proportions of dioxane and nitromethane showed that the trend is towards shorter induction periods and faster rates as the nitromethane content of the mixture is increased. It is thought that this trend is connected with the decreasing basicity of the medium rather than the increase in its dielectric constant.

It seemed most likely that the reaction was being initiated by the spontaneous production of an acid in the reaction mixture. The following tests were made which confirmed this belief. To a solution of 1-methylhepytl nitrite in 2-methyl-2-butanol was added just enough lacmoid indicator to give a recognizable color. This solution was divided

into two. One half was placed in the polarimeter and the rotation observed. After an induction period of about 5 hours reaction started and it was observed that the indicator had changed color. To the other half was added sodium 2-methyl-2-butoxide to give a concentration of about 10^{-4} *M*. This alkaline solution was further divided into two. After 24 hours both alkaline solutions were unchanged. One of these was then irradiated with a mercury lamp until the color changed; reaction began at once. Addition of just enough alkali to restore the indicator color immediately stopped the reaction.

From our other work (4) it is estimated that a concentration of approximately 10^{-6} *M* of a strong acid is all that is needed to account for the observed reaction rates. A weak acid, such as nitrous acid, would have to be present in very much higher concentrations, as was shown by the investigation of formic acid as a catalyst (4). A concentration of approximately 0.1 ***M*** of this acid, which is comparable in strength to nitrous acid, is needed to produce the observed rate. The most likely catalyst is nitric acid, which could be formed in sufficient quantity if traces of oxygen remained in the solutions or apparatus. The following is a possible reaction sequence;

$$\mathrm{RONO} \rightleftarrows \mathrm{RO}\cdot + \mathrm{NO} \quad \text{(thermal or photochemical decomposition (5))}$$

$$\mathrm{NO} + \mathrm{O} \rightarrow \mathrm{NO_2}$$

$$2\mathrm{NO_2} \rightleftarrows \mathrm{N_2O_4}$$

$$\mathrm{R'OH} + \mathrm{N_2O_4} \rightarrow \mathrm{R'ONO} + \mathrm{HNO_3}. \qquad (6)$$

It is also possible that a much more complex decomposition of the nitrite could produce nitric acid in the absence of oxygen (7). Under normal atmospheric conditions it is obvious that the above reactions could occur readily. The presence of nitric acid in samples of 1-methylheptyl nitrite that had been exposed to the atmosphere was demonstrated by the addition of a small amount of pyridine, which gave a fine white precipitate, m.p. 118°, which gave a positive test for nitrate ion and which did not depress the melting point of synthetic pyridinium nitrate. Samples of the nitrite prepared and preserved as described in the experimental section gave no precipitate with pyridine.

CONCLUSIONS

Our results show that the commonly observed 'uncatalyzed' reaction of an alkyl nitrite with alcohols is caused by traces of nitric acid arising from the thermal or photochemical decomposition of the nitrite in the presence of atmospheric oxygen. In acid-free solutions no reaction occurs. The results in alkaline solution show that the unprotonated ester molecule can only be attacked by strong nucleophilic reagents such as alkoxide, since no solvolytic component of the reaction rate could be detected. The mechanism of the reaction with alkoxide in alcoholic solution appears to be the same as that with hydroxide in aqueous solution, and involves a nucleophilic attack by alkoxide ion on the nitrogen atom of the nitrite molecule.

EXPERIMENTAL

Resolution of Octan-2-ol

Octan-2-ol was resolved into its (+) and (−) optical isomers by Kenyon's phthalic anhydride – brucine method (8). From several such resolutions the following average values were obtained: b.p. 86°/20 mm, $n_D^{25°}$ 1.4244, $[\alpha]_D^{25°}$ +9.53, −9.33°.

Preparation of (+)- and (−)-1-Methylheptyl Nitrite

These were prepared from the (+)- or (−)-octan-2-ol by esterification with nitrous

acid in weakly acid solution. The procedure of Chretien and Longi (9), using aluminum sulphate as the source of acid, was found to be greatly superior to the more commonly used methods. Yields were generally better than 90% if the temperature was kept below 5° throughout the preparation. The crude product was dried and fractionally distilled at reduced pressure in a nitrogen atmosphere, giving b.p. 61–62°/15 mm, 34°/2.5 mm, $n_D^{25°}$ 1.4067, $d_4^{25°}$ 0.8602, $[\alpha]_D^{25°} \pm 5.00°$ (mean value, no solvent). The pure product was stored over potassium carbonate in a dark flask at 0° to minimize decomposition.

Purification of Solvents

The solvents used were purified and thoroughly dried by standard procedures, and fractionally distilled at high reflux ratio using a 48-in. helix packed column. Purity and dryness were checked by constancy of the boiling point on changing to total reflux. The absence of water in the dried solvents was confirmed by Karl Fischer titration (10). All solvents were collected and stored in an atmosphere of dry nitrogen, and samples for use were taken by siphon, using dry nitrogen pressure.

Equilibrium Measurements

1-Methylheptyl nitrite was mixed with the appropriate alcohol. Acid was added and the change in rotation followed until a constant value was obtained. The rotation for 100% reaction was calculated and hence the position of equilibrium was found. The results are shown in Table IV.

TABLE IV

1-Methylheptyl nitrite:alcohol equilibria at 25°

$[R^*ONO]_0$ (M)	$[R'OH]_0$ (M)	α_D^{25} at t_∞ (observed)	α_D^{25} 100% (calculated)	% reaction	K_e
(*a*) R′OH = 2-methyl-2-butanol					
0.512	8.30	1.080	1.18	83.5	0.28
0.421	8.47	0.90	0.975	85.0	0.25
0.638	8.08	1.34	1.47	83.0	0.34
0.451	8.41	0.97	1.05	85.0	0.28
0.251	8.74	0.555	0.585	90.0	0.24
(*b*) R′OH = 2-propanol					
0.528	11.7	1.225	1.280	92.0	0.49
0.745	11.2	1.70	1.80	89.5	0.53
(*c*) R′OH = 1-propanol (in dioxane solution)					
0.522	1.3	1.21	1.50	78.5	1.6

NOTE: [Acid] = 10^{-3}–10^{-4} M.

Alkaline Alcoholysis

Stock solutions of sodium propoxide in 1-propanol were prepared by dissolving clean sodium in the dry alcohol, in an atmosphere of dry nitrogen. The solution was standardized against standard hydrochloric acid. The reagents for each kinetic run were separately brought to 25°, mixed at zero time, and transferred to the polarimeter tube under dry nitrogen. Details of a typical run were as follows:

$[R^*ONO]_0 = 0.596$ M $[\text{Propoxide}]_0 = 4.34 \times 10^{-2}$ M $\alpha_D^{25}(t = \infty, \text{calc.})$ 1.510

Time (min)	6	13	22	42	53	65	120	210	20 hours
α_D^{25} (obs.)	.74	.76	.78	.82	.83	.85	.94	1.06	1.465

$k_1 = 0.43 \times 10^{-4}$ sec^{-1} $k_2 = k_1/[RO^-]_0 = 9.9 \times 10^{-4}$ sec^{-1} M.$^{-1}$ l.

Alcoholysis in Neutral Solution

To obtain solutions free from acid and oxygen for this part of the work the following precautions were found to be necessary: (*a*) Small samples of 1-methylheptyl nitrite from stock preparations were freshly distilled from potassium carbonate in the dark at low pressures immediately before each kinetic run. Static distillation into a liquid-air trap at about 10^{-4} mm pressure was used, the distillate being collected in a calibrated tube and used immediately. (*b*) All operations were carried out in an atmosphere of dry nitrogen. (*c*) All solvents were thoroughly degassed and stored in an atmosphere of dry nitrogen. (*d*) The reaction mixture was shielded from light, except for occasional exposure to the sodium lamp during measurement of the rotation. In the following example an induction period of about 3 hours was observed. The first-order rate coefficient for the initial part of the reaction which followed was approximately 0.12×10^{-4} sec^{-1}.

$[R^*ONO]_0 = 0.856\ M$ Solvent: 2-methyl-2-butanol, 25°

Time (hr)	0	1	2	3	$4\frac{1}{2}$	5	$6\frac{3}{4}$	$7\frac{3}{4}$	∞ (calc.)
α_D^{25} (obs.)	0.95	.95	.945	.955	.985	1.005	1.07	1.125	1.96

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THE MECHANISM OF THE ALCOHOLYSIS OF ALIPHATIC NITRITES

II. ACID-CATALYZED ALCOHOLYSIS OF 1-METHYLHEPTYL NITRITE[1]

A. D. ALLEN[2] AND G. R. SCHONBAUM[3]

ABSTRACT

The acid-catalyzed alcoholysis of 1-methylheptyl nitrite has been studied kinetically. The reaction rate is first order with respect to both the nitrite and the hydrogen ion concentration, and the reaction does not involve the asymmetric carbon center. Addition of lithium salts (chloride and perchlorate) indicates catalysis by chloride ion. Addition of water in low concentrations inhibits the reaction strongly. These results and the mechanism of the reactions are discussed in terms of the properties of the alcohols and the dissociation of the acid catalysts in the alcohols used.

In a previous paper (1) it was reported that the alcoholysis of 1-methylheptyl nitrite in "neutral" solution was, in fact, catalyzed by traces of a strong acid, probably nitric acid, formed in the decomposition of the nitrite ester. The sensitivity of this reaction to very small concentrations of acid led to a study of the mechanism of the acid-catalyzed reaction.

The polarimetric method was again used, and the alcoholysis of (+)- or (−)-1-methylheptyl nitrite in 1-propanol, 1-pentanol, and 2-methyl-2-butanol was studied, using various acids as catalysts.

Catalysis by Strong Acids

In very dilute solutions of perchloric, hydrochloric, or methanesulphonic acid the reaction rate was found to be first order with respect to both the acid and ester concentration, giving the rate expression $v = k_2[H^+][R^*ONO]$ (R*— = (+)- or (−)-1-methylheptyl-). Since the hydrogen ion concentration was constant during each kinetic run, first-order kinetics were observed, the first-order rate coefficient being proportional to the acid concentration. The reagent alcohol was in large excess over the other reagents and does not, therefore, appear in the rate equation. A comparison of the results obtained in 1-propanol with the three strong acids used is shown in Table I.

TABLE I

Catalysis by strong acids in 1-propanol at 25°

(*a*) Hydrochloric acid							
[HCl] 10^5 *M*	3.60	5.26	6.30	8.30	10.70	12.20	13.0
$10^4 k_1$ sec^{-1}	3.6	5.5	7.1	8.9	12.8	14.6	15.5
k_2 sec^{-1} M.$^{-1}$ l.	10.0	10.4	11.3	10.7	12.0	12.0	11.9
(*b*) Perchloric acid							
[$HClO_4$] 10^5 *M*	1.70	5.35	8.10	8.85	11.4	12.5	
$10^4 k_1$ sec^{-1}	1.82	5.55	8.7	9.45	14.1	14.2	
k_2 sec^{-1} M.$^{-1}$ l.	10.7	10.4	10.7	10.7	12.4	11.4	
(*c*) Methanesulphonic acid							
[Acid] 10^5 *M*	3.05	4.50	6.05	8.40	9.35		
$10^4 k_1$ sec^{-1}	3.12	4.55	7.30	8.95	10.95		
k_2 sec^{-1} M.$^{-1}$ l.	10.2	10.1	12.0	10.6	11.4		

NOTE: $[R^*ONO]_0 \simeq 0.5$ *M*.

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It is evident that perchloric, hydrochloric, and methanesulphonic acids are equally efficient as catalysts for the reaction. This indicates that, in 1-propanol at these very low (10^{-4}–10^{-5} *M*) concentrations, all three acids are virtually completely dissociated. It also follows that the hydrogen ion is the only significant catalyst, since changes in the nature of the anion do not affect the rate. Previously (2) we observed catalysis of the hydrolysis reaction by halide ion in aqueous dioxane, resulting in faster rates in hydrochloric acid than in perchloric acid solutions of the same concentration. In the present case, however, the acid concentrations are very much smaller and it is probable that any catalysis by chloride ion would be too small to be detected. The effect of added chloride ion will be discussed later.

In 1-pentanol and the tertiary alcohol 2-methyl-2-butanol a similar dependence of rate on acid concentration was observed. The results obtained are given in Table II.

TABLE II

Catalysis by perchloric acid in 1-pentanol and 2-methyl-2-butanol at 25°

1-Pentanol			2-Methyl-2-butanol		
[Acid] 10^5 *M*	$10^4 k_1$ sec^{-1}	k_2 sec^{-1} M.$^{-1}$ l.	[Acid] 10^5 *M*	$10^4 k_1$ sec^{-1}	k_2 sec^{-1} M.$^{-1}$ l.
5.91	6.30	10.6	1.80	4.00	22.2
7.06	8.01	11.2	3.90	8.65	22.2
10.6	13.2	12.4	5.0	10.95	21.9
15.1	17.8	11.8	8.1	17.1	20.9
			12.8	26.8	21.0

NOTE: $[R^*ONO]_0 \simeq 0.5$ *M*.

The rate of the reaction with the tertiary alcohol is about twice as fast as that with the two primary alcohols. The mechanism appears to be the same in each case, and is also the same as that observed in aqueous dioxane (2). The rate-determining step is preceded by a proton transfer equilibrium:

$$R^*ONO + SH^+ \overset{\text{fast}}{\rightleftharpoons} (R^*ONOH)^+ + S, \qquad (S = \text{solvent})$$

which is established rapidly and is maintained throughout the reaction. This is followed by the rate-determining step:

$$(R^*ONOH)^+ + R'OH \overset{\text{slow}}{\rightleftharpoons} (R'ONOH)^+ + R^*OH.$$

For this we envisage a bimolecular nucleophilic attack by the alcohol on the nitrogen atom of the protonated ester, preserving the configuration of the asymmetric carbon center:

$$R'OH + (R^*ONOH)^+ \underset{\text{fast}}{\overset{\text{slow}}{\rightleftharpoons}} \left[R'\overset{H}{O} \ldots \overset{O}{\overset{\|}{N}} \ldots \overset{H}{O}R^* \right]^+ \underset{\text{slow}}{\overset{\text{fast}}{\rightleftharpoons}} (R'ONOH)^+ + R^*OH.$$

Two important factors will influence the rate of this reaction, (*a*) the nucleophilic power of the reagent alcohol, and (*b*) the concentration of the protonated ester. The nucleophilic power of the alcohols used decreases in the order 1-propanol ~ 1-pentanol > 2-methyl-2-butanol, steric factors being the main reason for the relatively weak nucleophilic power of the tertiary alcohols. If this were the only factor it would result in a

much slower rate in the tertiary alcohol, contrary to our observations. To explain the observed faster rate we propose that, at equivalent acid concentrations, the concentration of the protonated ester is much greater in 2-methyl-2-butanol than in the primary alcohols. This means that the equilibrium:

$$R^*ONO + R'OH_2^+ \rightleftarrows R^*ONOH^+ + R'OH$$

is displaced to the right when R′ changes from primary to tertiary. Thus the tertiary alcohol is apparently much more weakly basic than the primary alcohol, despite the obvious inductive effects of the tertiary amyl group. There is much evidence to support this view. Absence of significant hydrogen bonding in liquid 2-methyl-2-butanol has been shown by infrared and dipole moment studies (3, 4). The relation between hydrogen bonding and basicity has been studied by Gordy and Stanford (5, 6), who found that the shift to lower frequencies of an infrared band of CH_3OD, due to deuterium bonding, is proportional to the basicity of the solvent used. The available data (7, 8) indicate that the basicity of hydroxy compounds decreases in the order: water $\gg$ primary $>$ secondary $>$ tertiary alcohols. It should be noted that this sequence is quite different from the order of relative basicities of the corresponding alkoxides, illustrating the importance of steric strain in the protonated molecule, ROH_2^+ (8, 9).

Catalysis by Organic Acids

As part of the investigation into the cause of the so-called "neutral" reaction, a study was made of the catalytic effect of trichloroacetic and formic acids. Reaction rates in 1-propanol and 2-methyl-2-butanol, in the presence of trichloroacetic acid, are shown in Table III.

TABLE III

Catalysis by trichloroacetic acid at 25°

1-Propanol			2-Methyl-2-butanol		
[Acid] 10^3 *M*	$10^4 k_1$ sec^{-1}	$10^2 k_2$ sec^{-1} M.$^{-1}$ l.	[Acid] 10^3 *M*	$10^4 k_1$ sec^{-1}	$10^2 k_2$ sec^{-1} M.$^{-1}$ l.
1.31	1.11	8.5	2.90	0.94	3.2
2.84	2.27	8.0	5.40	1.75	3.2
3.75	3.02	8.1	8.40	2.82	3.4
5.41	4.54	8.4			

NOTE: $[R^*ONO]_0 \simeq 0.5$ *M*.

In both alcohols the rates are again first order with respect to both the ester and acid concentrations. For a given acid concentration, however, the rate is some 100 times slower than that found when the catalyst is a strong acid. This shows that trichloroacetic acid is only weakly ionized in these solvents, as would be expected. The faster rate in 1-propanol than in 2-methyl-2-butanol (in contrast to the previous results with strong acids) is readily explained on the basis of greater acid ionization in the medium of higher dielectric constant. The linearity of the dependence of rate on acid concentration is, however, surprising. From mass law considerations, we would expect a deviation from linearity due to a decrease in the degree of dissociation of the weak acid with increasing concentration. This will only be found, however, if the acid dissociation constant is independent of concentration. In solvents of moderately low dielectric constant, such as these alcohols, an increase in acid concentration has a marked effect on the activity

coefficient of the ionic species, resulting in an increase in the classical dissociation constant of the acid. For example, the dissociation constant for iodic acid (which is similar to that of trichloroacetic acid) in methanol increases from 2.4 to 14×10^{-8} when the acid concentration is raised from 9 to 64×10^{-4} M (10). It appears that a similar increase occurs with trichloroacetic acid in the alcohols used in our experiments, and that the linearity between rate and acid concentration is fortuitous. Assuming that hydrogen ion is the only catalyst, we can calculate the following dissociation constants (K_c) for trichloroacetic acid in these solvents at 25°.

[Acid] 10^3 M	1-Propanol 10^8 K_c	2-Methyl-2-butanol 10^8 K_c
1	8.1	—
3	19	0.83
5	31	—
6	—	1.5
9	—	2.2

A value of $K_c=34\times10^{-8}$ has been given (11) for this acid in 1-butanol at 25°, which is in good agreement with our results.

Formic Acid Catalysis

In 2-methyl-2-butanol the addition of formic acid in concentrations up to 0.01 M gave no measurable initial reaction. At 0.1 M acid concentration reaction occurred with a first-order rate coefficient of 0.29×10^{-4} sec^{-1}. Thus formic acid is about 100 times less effective as a catalyst than trichloroacetic acid. This is approximately the figure that would be expected if hydrogen ion were the only catalyst, bearing in mind the increase in the dissociation constant of formic acid at the very much higher concentrations used. The results with trichloroacetic and formic acids indicate that catalysis by the undissociated acid is negligible, even, in the case of formic acid, at concentrations of some 10^5 times greater than that of the hydrogen ion concentration. It also follows that, since formic acid is comparable in strength to nitrous acid, the spontaneous "neutral" reaction is not caused by traces of nitrous acid in the reaction mixture.

Salt Effects: (1) Strong Acids

The effect of added salts (lithium perchlorate and lithium chloride) on the reactions catalyzed by hydrochloric and perchloric acids in 1-propanol are given in Table IV.

TABLE IV

Salt effects on catalysis by strong acids at 25°
$[R^*ONO]_0 \simeq 0.6$ M; $[HClO_4] = 6.5\times10^{-5}$ M; solvent: 1-propanol

Lithium chloride		Lithium perchlorate	
[Salt] 10^3 M	10^4 k_1 sec^{-1}	[Salt] 10^3 M	10^4 k_1 sec^{-1}
0	7.0	0	7.0
.99	10.2	3.11	9.9
1.44	11.6	4.69	11.0
2.52	13.1	6.70	11.2
4.10	14.4		
4.72	14.6		
9.02	14.5		

Lithium chloride has a much greater effect on the rate than lithium perchlorate, but the increase in rate is not linear with respect to concentration. The rate reaches a maximum value at about 4×10^{-3} *M* chloride ion, i.e. at about 60 times the concentration of acid used. It is not possible, on the basis of these few results, to attempt a full analysis of these salt effects, but the results are at least consistent with (*a*) significant catalysis by chloride ion, as observed in hydrolysis, and (*b*) depression of the hydrogen ion concentration by its association with chloride ion to form hydrogen chloride. The results obtained are consistent with a dissociation constant of between $3\text{–}4\times10^{-3}$ for hydrogen chloride in this medium. Owen and Waters (12) give a value of 2×10^{-4} for this acid in 82% dioxane–water, which has a lower dielectric constant than 1-propanol.

Salt Effects: (2) Trichloroacetic Acid

Addition of lithium chloride and lithium perchlorate to reactions catalyzed by trichloroacetic acid in 1-propanol and 2-methyl-2-butanol gave the following results (Table V).

TABLE V

Salt effects on catalysis by trichloroacetic acid at 25°

1-Propanol				2-Methyl-2-butanol			
[Acid] = 2.5×10^{-3} *M*				[Acid] = 2.8×10^{-3} *M*			
[LiCl] 10^3 *M*	$10^4 k_1$ sec^{-1}	[$LiClO_4$] 10^3 *M*	$10^4 k_1$ sec^{-1}	[LiCl] 10^3 *M*	$10^4 k_1$ sec^{-1}	[$LiClO_4$] 10^3 *M*	$10^4 k_1$ sec^{-1}
0	2.10	0	2.10	0	0.95	0	0.95
0.98	3.60	1.68	3.75	0.50	4.67	0.79	1.85
1.70	4.95	3.03	4.90	1.01	7.45	1.61	2.15
2.42	6.25	4.16	6.15	1.26	10.55	2.32	3.20
				1.62	12.5	2.95	3.75

NOTE: $[R^*ONO]_0 \simeq 0.5$ *M*.

Addition of lithium perchlorate produces an increase in rate in both alcohols, the relative increase being greater in the tertiary alcohol. These increases are presumably due to an increase in the dissociation of the weak acid with increasing ionic strength of the medium, and would be expected to be greater in the medium of lower dielectric constant.

Addition of lithium chloride produces a greater effect in both solvents, but the effect is particularly marked in the tertiary alcohol. This is consistent with catalysis by chloride ion, which would be greater in the system involving the combination of a greater concentration of the protonated ester and a weaker nucleophilic reagent. It was argued earlier that the reaction in the tertiary alcohol fulfills both these requirements in comparison with the reaction in the primary alcohol.

Effect of Added Water on the Acid-Catalyzed Reaction

The difference in the rates of the acid-catalyzed reactions in the primary and tertiary alcohols was attributed to a marked difference in the basicity of the reagents. If this is so, then the addition of a small amount of a very much more basic substance to the reaction mixture should decrease the rate strongly, and should have the most marked effect on the system involving the weakest base. Since water is very much more basic

than these alcohols, addition of small amounts of water to the reaction mixture will set up the following equilibria, which will be displaced strongly towards the right:

$$R'OH_2^+ + H_2O \rightleftarrows R'OH + H_3O^+,$$

$$R^*ONOH^+ + H_2O \rightleftarrows R^*ONO + H_3O^+.$$

Thus addition of water should result in a decrease in the concentration of the protonated nitrite, which will retard the reaction rate strongly, provided that the concentration of water is sufficiently low to prevent its being able to act significantly as a nucleophilic reagent. In this connection it has been shown (10) that addition of water to dilute alcoholic solutions of strong acids decreases the conductivity, the decrease being linear with water concentration up to about 1% water, above which concentration the conductivity begins to increase.

The effect of addition of small amounts of water on the reaction in 1-propanol, 1-pentanol, and 2-methyl-2-butanol, catalyzed by perchloric acid, is shown in Fig. 1.

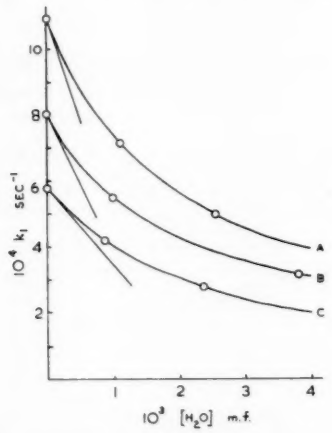

FIG. 1. Effect of added water on acid catalysis. First-order rate constants at 25° in A = 2-methyl-2-butanol, B = 1-propanol, and C = 1-pentanol, at constant (5.66×10^{-6}) acid mole fraction.

Significant decreases in rate were observed even at very low (10^{-3} *M*) concentrations of water. From the smooth curves obtained it is possible to estimate the slope at zero water concentration. The steepest slope occurs with the least basic alcohol, 2-methyl-2-butanol, and it appears that 1-pentanol is more basic than 1-propanol. These results, together with the effects of added salts, provide strong support for the argument that the basicity of the reagents is one of the important factors in these reactions. They also emphasize the importance of carrying out any alcoholysis reaction rate studies in perfectly dry solvents, since random traces of water would completely invalidate any results obtained.

EXPERIMENTAL

(1) Materials

Octan-2-ol was resolved into its (+) and (−) optical isomers, (+)- and (−)-1-methylheptyl nitrite was prepared and purified, and all solvents and reagents were purified and dried as described previously (1).

(2) Optical Rotations of Reaction Mixtures

The results previously reported (1) were used to determine the progress of the various reactions from changes in optical rotation and in the calculation of rate constants.

(3) Kinetic Measurements

All operations were carried out in an atmosphere of dry nitrogen. The (+)- or (−)-1-methylheptyl nitrite and the reagent alcohol were separately brought to thermostat temperature (25°) and then mixed. After allowing 1–2 minutes to regain thermostat temperature the appropriate acid solution was added at zero time. The mixture was then transferred rapidly to the polarimeter tube, using a self-sealing rubber diaphragm cap. Changes in optical rotation (sodium D line) with time were observed, the following being typical examples:

Example 1

$[R^*ONO]_0 = 0.560\ M$ $[HCl] = 5.26\times10^{-5}\ M$ 25° Solvent = 1-propanol

Time (min)	2	4	6	8	10	15	20	25	30	40	∞
α_D	.700	.755	.800	.840	.895	.960	1.035	1.085	1.135	1.24	1.42

$k_1 = 5.48\times10^{-4}\ sec^{-1}$

Example 2

$[R^*ONO]_0 = 0.574\ M$ $[HClO_4] = 6.60\times10^{-5}\ M$ 25° Solvent: 2-methyl-2-butanol

Time (min)	2½	4	6	8	10	12	17	21	50	∞
α_D	.805	.865	.940	.995	1.045	1.075	1.145	1.170	1.220	1.220

$k_1 = 15.5\times10^{-4}\ sec^{-1}$

Example 3

$[R^*ONO]_0 = 0.611\ M$ $[HClO_4] = 6.20\times10^{-5}\ M$ $[H_2O] = 0.047\ M$ 25° Solvent: 1-propanol

Time (min)	2¼	4	9	15½	22	30	45	60	73	∞
α_D	0.735	.78	.85	.925	.995	1.075	1.185	1.280	1.335	1.545

$k_1 = 3.07\times10^{-4}\ sec^{-1}$

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ISOTOPE EFFECTS IN CARBONIUM ION REACTIONS
V. SOLVOLYSIS OF METHYL AND ETHYL *p*-BROMOBENZENESULPHONATES

EDWARD S. LEWIS, JUDITH C. BROWN, AND WILLIAM C. HERNDON

It has been suggested that various secondary hydrogen isotope effects in solvolytic reactions are related to changes in hyperconjugation (1), to alterations in vibrational frequencies on change of hybridization (2), and to changes in extent of non-bonded interactions (3) on activation. Among the data leading to these conclusions were those showing solvent dependence of the effect of β-hydrogens on solvolysis rates (4). The reverse hydrogen isotope effects (5) in the reactions of methyl esters were attributed to increases in bending force constants resulting from steric interactions of the methyl hydrogens with the attacking and leaving groups, and this suggestion was supported by more extensive studies on the reactions of methyl halides in water (6).

Table I shows some rates and isotope effects for the solvolysis of methyl and ethyl

TABLE I

Isotope effects in solvolysis of methyl and ethyl *p*-bromobenzenesulphonates

Alkyl group*	Solvent	Temp., °C	$k_H \times 10^5$ sec^{-1}	k_H/k_D
CD_3CH_2†	CH_3CO_2H	116.8	10.56	1.01
CH_3CD_2‡	CH_3CO_2H	100	2.72	1.09±.03
CH_3CD_2‡	CH_3OH	56.2	3.25	1.04±.01
CD_3	CH_3CO_2H	100	2.66	0.92±.03
CD_3§	CH_3OH	70.25	25.13‖	0.940‖

*Alkyl groups are shown with deuterium. Reference compounds for which k_H is reported are normal methyl or ethyl *p*-bromobenzenesulphonates. †Deuterium analysis not precise, at least 75% deuterated. ‡Deuterium analysis not precise, almost no CH_3 n.m.r. spectrum visible. §2.88 D per molecule by mass spectra. ‖R. R. Johnson. Ph.D. Thesis, William M. Rice University, Houston, Texas, 1958, and ref. 5.

p-bromobenzenesulphonates in two solvents of widely differing nucleophilic character. These results can be shown to be consistent with explanations in terms of either electronic or essentially steric factors. We need only assume that there is virtually no carbonium ion character in any methyl ester solvolytic transition state, but that the transition state for the ethyl compound has a little carbonium ion character in acetic acid but less in the more nucleophilic methanol. This assumption then leads to the prediction that the isotope effect with methyl *p*-bromobenzenesulphonate will be insensitive to solvent, whereas in the ethyl case the value of k_H/k_D should increase as the nucleophilic character of the solvent decreases. The values in the table, although not highly precise, support this idea. The very small effect on β-substitution also is consistent with only minor carbonium ion character, even in acetic acid. This result is the same as that reported recently for water solutions (7).

EXPERIMENTAL

Materials

Ethyl *p*-bromobenzenesulphonate was prepared from the alcohol by conventional procedures (8). Ethanol-2-d_3 was prepared by the lithium aluminum hydride reduction of sodium acetate-d_3 (Isotopes Specialties Corp.). A rather crude deuterium analysis by

combustion indicated 75% D in the β-position, but the n.m.r. spectrum indicated a much larger extent of deuteration.

Ethanol-1-d_2 was prepared by the reduction of cyclohexyl acetate with sodium and acetic acid-*d* in dibutyl ether (9). Infrared and n.m.r. showed nearly complete deuteration, but the exact extent is not established.

Methyl-d_3 *p*-bromobenzenesulphonate was prepared by R. R. Johnson, by the sequence

$$\text{methyl bromide-}d_3\ (10) \xrightarrow[\text{acetone}]{\text{NaI}} \text{methyl iodide-}d_3 \rightarrow \text{methyl-}d_3\ p\text{-bromobenzenesulphonate,}$$

using silver *p*-bromobenzenesulphonate. It was the same material reported in ref. 5.

Rate Measurements

All rates were measured by titration of the acid produced using an electrometric end point by familiar methods. Solvents were Reagent Grade materials and the hydrogen and deuterium compounds were run concurrently to avoid errors attributable to variations in water content of the solvents, thermostat temperatures, and the clock. The rates in Table I are therefore not known absolutely as well as are the isotope effects. All entries are the averages of at least two runs, agreeing in isotope effect within the estimated precision.

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ARSENIDES OF THE TRANSITION METALS
IV. A NOTE ON THE PLATINUM METAL ARSENIDES*

R. D. Heyding and L. D. Calvert

In the current literature increasing attention is given to the binary compounds formed by the VA elements (pnigogens†) and the platinum metals. Rundqvist has undertaken a systematic study of the phosphides (1), and Zhuravlev and Zhdanov the antimonides and bismuthides (e.g., 2, 3, 4). To our knowledge there are no reports on the formation and structure of platinum metal arsenides, with the exception of Thomassen's early study of palladium and platinum arsenides (5), Schubert's recent note on the compound Pd_3As

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†*The terms pnigogen and pnictide have been suggested by Prof. A. E. van Arkel for the elements and compounds of the nitrogen family, N, P, As, Sb, and Bi. The root is the Greek word to choke, and the allusion to the Germanic name for nitrogen, Stickstoff, or choking gas.*

(6), and Kjekshus' redetermination of the unit cell dimensions of $PtAs_2$ (7). We have prepared binary alloys corresponding to M_3As, M_2As, MAs, MAs_2, and MAs_3 with all of the platinum metals, and have examined their structures by X-ray powder diffraction techniques. The results of this preliminary survey are reported here.

All alloys were formed by reaction of the elements in sealed vycor tubes at 700° C in the usual manner. High-purity metal sponge was obtained from Baker Platinum, and semiconductor grade arsenic from ASARCO and COMINCO. The products were ground and annealed for a minimum of 2 days at 700° C and cooled slowly to room temperature. Debye–Scherrer patterns were obtained in 11-cm Norelco cameras using copper K_α radiation.

Two compounds are formed in the ruthenium/arsenic system: RuAs, with the orthorhombic B31 (MnP) structure, and $RuAs_2$, with the orthorhombic C18 (marcasite) structure. With the single annealing scheme followed no other compounds could be detected.

$OsAs_2$, also with the marcasite structure, was the only compound observed in the osmium/arsenic system.

At least four compounds are formed in the rhodium/arsenic system: The compound Rh_2As has the f.c.c. C1 (antifluorite) structure; RhAs, the orthorhombic B31 structure; and $RhAs_3$ the cubic DO_2 (skutterudite) structure. The structure of the fourth compound, $RhAs_2$, is complicated and as yet unknown.

Iridium and arsenic form $IrAs_3$ with the cubic DO_2 structure. In this system there are two other phases, the diarsenide $IrAs_2$ whose structure has not been determined, and apparently one other compound in the composition region between $IrAs_2$ and $IrAs_3$.

There are at least two compounds in the palladium/arsenic system. Pd_3As has the b.c. tetragonal Fe_3P structure, which confirms Schubert's description, and $PdAs_2$ has the cubic C2 (pyrite) lattice, in agreement with Thomassen's data. A complicated series of phases has been observed in the region between Pd_3As and Pd_2As.

Only one compound has been obtained in the platinum/arsenic system, $PtAs_2$ with the C2 structure, again in agreement with Thomassen's data.

Unit cell dimensions for the compounds whose structures have been identified are given in Table I.

TABLE I

Structures and unit cell dimensions of platinum metal arsenides

Structure type	Compound	a (Å)	b (Å)	c (Å)	Ref.
Tetragonal DO_a (Fe_3P) S_4^2, $I\bar{4}$	Pd_3As	$9.95_1\pm0.01$ (9.98_6)		$4.81_7\pm0.01$ (4.83_6)	(6)
Cubic C1 (antifluorite) O_h^5, $Fm3m$	Rh_2As	5.674 ± 0.001			
Rhombic B31 (MnP) V_h^{16}, $Pnma$	RuAs RhAs	5.70 ± 0.01 5.62 ± 0.01	3.25 ± 0.01 3.58 ± 0.01	6.27 ± 0.01 6.00 ± 0.01	
Rhombic C18 (marcasite) V_h^{12}, $Pnnm$	$RuAs_2$ $OsAs_2$	5.41 ± 0.01 5.40 ± 0.01	6.17 ± 0.01 6.16 ± 0.01	2.96 ± 0.01 3.00 ± 0.01	
Cubic C2 (pyrite) T_h^6, $Pa3$	$PdAs_2$	5.983 ± 0.001 (5.970)*			(5)
	$PtAs_2$	5.966 ± 0.001 (5.957)* (5.9665)			(5) (7)
Cubic DO_2 (skutterudite) T_h^5, $Im3$	$RhAs_3$ $IrAs_3$	8.453 ± 0.001 8.467 ± 0.001			

*Thomassen's values are probably in kX units.

It is remarkable that all of the 1:1 compounds crystallize in the distorted NiAs (MnP) structure rather than the NiAs structure itself. In the palladium and platinum systems where one might anticipate the NiAs structure no 1:1 compounds were obtained.

The diphosphides, diarsenides, and diantimonides of ruthenium and osmium have the marcasite structure, while the corresponding compounds of palladium and platinum have the pyrite structure. The rather complicated diffraction patterns of $RhAs_2$ and $IrAs_2$ are most certainly related, and bear a distinct similarity to the pattern of $CoAs_2$ (8). A strong low-order reflection in the $CoAs_2$ pattern is split in the $RhAs_2$ and $IrAs_2$ patterns; this leads us to doubt the orthorhombic cell we proposed earlier for $CoAs_2$. These diarsenides may prove to be isostructural with the rhodium and iridium diphosphides mentioned by Rundqvist.

Since the triphosphides and triantimonides of cobalt, rhodium, and iridium are known to have the cubic $CoAs_3$ structure, it is not surprising that $RhAs_3$ and $IrAs_3$ have the same structure. The list of compounds crystallizing in the skutterudite system now stands at 11, and insofar as binary pnictides are concerned, can be considered to be complete. With the exception of NiP_3 and PdP_3 they are formed only by the cobalt family of transition metals. Bismuthides with this structure have not been observed.

These systems are now being studied in some detail.

We are indebted to Miss M. McClellan and Mr. G. J. G. Despault for their assistance in preparing alloys and obtaining diffraction patterns.

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SOLVATION EFFECTS AND RELATIVE RATES
III. SALT EFFECTS IN THE SOLVOLYSIS OF exo-NORBORNYL BROMIDE*

Kirk D. McMichael and Robert A. Clement

As part of our study of solvation effects in organic reactions (1, 2), it seemed desirable to examine the nature of the kinetic salt effect for a simple organic reaction in a typical organic solvent. The system we chose for study was exo-norbornyl bromide in 85% (w/w) aqueous dioxane at 25.06°, and our approach was that used in an earlier paper (1) in which analysis of kinetic and thermodynamic data is in terms of the Bronsted rate law (3).

**This paper is abstracted from a portion of the Ph.D. dissertation of Kirk D. McMichael, University of Chicago, 1960, and was presented before the Organic Division, American Chemical Society, at the 138th National Meeting, New York, September 11–16, 1960.*

Existing information (4, 5) on the solvolyses of exo-norbornyl derivatives indicates the operation of unimolecular reactions possibly complicated, however, by internal return from a reactive ion-pair intermediate. Hence, the appropriate form of the Bronsted rate law for the system under study is equation [1] (1, 6)

$$k'/k = (H'/H)F$$

where k is the observed first-order specific rate constant for the production of acid, H is the Henry's law constant for distribution of exo-norbornyl bromide between the solution and the gas phase, F is a factor of constitution dependent upon the precise course of reaction (1), the primed symbols refer to a salt solution, and the unprimed symbols to the reference solution, the pure solvent. The ratio k'/k is the total kinetic salt effect and the ratio H'/H is that portion of the kinetic salt effect due to the influence of salt on the activity coefficient of the substrate. It is the factor F, alone, which yields information on the effect of salt upon the stability(ies) of the critical complex(es); in general, it will be greater than unity if salt stabilizes the critical complex(es) and less than unity if salt destabilizes the critical complex(es).

In the present study, initial first-order specific rate constants, k, for the production of strong acid were obtained for solutions of exo-norbornyl bromide in 85% (w/w) aqueous dioxane in the absence of salt and in the presence of lithium chloride, bromide, and perchlorate and sodium perchlorate at concentrations of 0.100 M and of magnesium perchlorate at a concentration of 0.0333 M. The results are recorded in Table I. From

TABLE I

First-order specific rate constants for the development of acid, Henry's law constants for exo-norbornyl bromide, and related data for exo-norbornyl bromide in 85% (w/w) aqueous dioxane at 25.06° in the presence of various salts at ionic strengths of 0.100 molar

Salt	$10^5\,k$, sec^{-1}	H, $mm(mole/L.)^{-1}$	p_{H_2O}, mm	$p_{dioxane}$, mm	k'/k	H'/H	F
None	3.57	0.72	18.5	29.1	(1.000)	(1.000)	(1.000)
LiCl	5.0	0.68	17.7	29.4	1.40	0.94	1.49
LiBr	5.2	0.69	17.9	29.4	1.46	0.96	1.52
$LiClO_4$	7.4	0.72	18.1	29.2	2.07	1.00	2.07
$NaClO_4$	7.0	0.71	18.1	29.0	1.96	0.99	1.98
$Mg(ClO_4)_2$	6.2	0.70	18.1	29.0	1.74	0.97	1.80

the ratios k'/k it is apparent that the solvolysis of exo-norbornyl bromide in this solvent is subject to very large kinetic salt effects.

Henry's law constants, H, for the distribution of exo-norbornyl bromide between the vapor phase and the same solutions utilized for the kinetic experiments were obtained by the dynamic vapor pressure technique essentially as described earlier (2), and are also recorded in Table I. The Henry's law constant for exo-norbornyl bromide in this solvent is *essentially insensitive to the presence of salts.*

Although irrelevant to the use of equation [1], the vapor pressures of water (p_{H_2O}) and of dioxane ($p_{dioxane}$) above the various solutions were obtained, necessarily, during the measurements of the Henry's law constants and are recorded in Table I. They are also insensitive to the presence of salts.

Consideration of the entries in Table I in terms of equation [1] shows clearly that for the solvolysis of exo-norbornyl bromide in 85% (w/w) aqueous dioxane the kinetic salt effect is due, almost exclusively, to the factor F. In this system, then, it is proper to

regard the kinetic salt effect as a reflection of the nature of the critical complex(es), and the usual qualitative deduction that a positive kinetic salt effect identifies a critical complex that is more ionic than the reactant is completely justified.

It should be noted that the result of this study stands in marked contrast to the results of previous studies (1, 6, 7, 8, 9, 10, 11) where, in every case, the ratio H'/H was found to make a significant contribution to the over-all kinetic medium effect, k'/k. Further investigation is necessary to ascertain whether this result is general for reactions in mixed aqueous–organic media or is due to a peculiarity of the present system.

EXPERIMENTAL

Kinetic and thermodynamic measurements were made at a temperature of 25.06+0.02° as established by an N.B.S.-calibrated thermometer.

Materials

Anhydrous salts were prepared from commercial reagent-grade materials which were dried to constant weight in an oven at the appropriate temperatures and were stored in a desiccator over anhydrous magnesium perchlorate.

Dioxane was purified by the method of Fieser (12) and was stored frozen, in the dark and under nitrogen, in glass-stoppered bottles which were sealed with paraffin.

exo-Norbornyl bromide (exo-2-bromobicyclo[2.2.1]heptane) was prepared by the method of Roberts (13) from purified norbornene, m.p. 43–44°, sealed cap. (lit. (14) m.p. 44–46°). In order to remove reactive impurities, the exo-norbornyl bromide (b.p. 81.0–81.8° (30 mm)) obtained initially was mixed with ethylene glycol and heated on the steam bath for 20 minutes, at the end of which ca. 25% (by acidimetry) of the bromide had been destroyed. The mixture was then poured into water, the organic layer was isolated, washed twice with water, and dried over magnesium sulphate. Distillation afforded pure exo-norbornyl bromide, b.p. 78.7–79.5° (29 mm), n_D^{25} 1.5124 (lit. (13) b.p. 82° (29 mm), n_D^{25} 1.5126). The kinetic homogeneity of the material was demonstrated by solvolysis of a sample in 80% (v/v) aqueous ethanol at the boiling point of acetone. Precise conformation to first-order kinetics was observed with a specific rate constant of 5.3×10^{-5} sec^{-1} (lit. (15) $k = 5.6\times10^{-5}$ sec^{-1} at 55°) and an experimental infinity titer (10 half lives) 98% of the calculated value.

Kinetic and Vapor Pressure Measurements

Kinetic and vapor pressure measurements were made in tandem on portions of the same solution which was prepared by diluting to volume with freshly prepared solvent (85 parts of dioxane and 25 parts of water, by wt.) weighed amounts of exo-norbornyl bromide and anhydrous salt. The final solutions were all 0.100±0.001 M in exo-norbornyl bromide and the salt solutions possessed molar ionic strengths of 0.100±0.001. Solvent was prepared as required for each run, and as a check on the reproducibility of its composition, the kinetic behavior of exo-norbornyl bromide was determined in each preparation; the average deviation of the first-order specific rate constants obtained from 12 such determinations was less than 2%.

The rate of development of strong acid was followed titrimetrically as before (2), the reactions being followed to 1.5–5% completion. First-order specific rate constants were determined by the increment method (1), plotted vs. % reaction and extrapolated back to 0% to yield the initial first-order specific rate constants, k, reported in Table I. Each k in Table I is the average of at least two runs involving different batches of solution and possesses an average deviation of 2–4%. The slopes of the plots of the first-order

specific rate constants vs. % reaction were all close to zero, and in most cases the average rate constant was within the limits defined by the average deviation of the extrapolated value.

Vapor pressure measurements were made by the dynamic method essentially as described before (2) except that nitrogen was the entraining gas and that mass flow was induced by a hydrostatic head of mercury which could not exceed 1 mm. The contents of the distillate trap was analyzed for exo-norbornyl bromide by precipitation of silver bromide with acidic aqueous ethanolic silver nitrate and for water by the Karl Fischer technique; dioxane was determined by difference. The values of the Henry's law constant, H, for exo-norbornyl bromide, and of the partial pressures of water, p_{H_2O}, and of dioxane, $p_{dioxane}$, obtained for each solution are recorded in Table I as the averages of at least two separate determinations which involved different flow rates (6.5–9.5 l./hr) of the entraining gas and different batches of solution. The average deviations noted were 1–2%.

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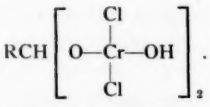
KINETICS OF ETARD'S REACTION

R. A. STAIRS AND J. W. BURNS*

The oxidation of toluene and similar compounds to aldehydes by chromyl chloride has been known (1) since Etard's work (1877–1893, see reference 2) but has never been thoroughly understood. It is characterized by the formation of a brown, insoluble substance, readily hydrolyzed to the aldehyde (and inorganic substances). Etard formulated the precipitate:



Note that the oxidation state of chromium is IV (see ref. 7). This structure has been much criticized, but never discredited.

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Some mechanisms have been proposed (3, 4) for other reactions of chromyl chloride, but no work has been done on the kinetics or the mechanism of the Etard reaction proper. The present note records an attempt to fill this gap.

EXPERIMENTAL

Three compounds were chosen that were expected to show significant differences in rate. They were toluene, diphenylmethane (which yields benzophenone), and triphenylmethane (which yields triphenylcarbinol). In addition one run was done with benzyl chloride. Carbon tetrachloride was the solvent.

The reactions were carried out in 10 or 12 Hinton flasks. The flasks were supported on a simple stand in a thermostat. Aliquot portions of chromyl chloride solution were pipetted into one compartment of each flask, the other reactant into the other, and the flasks stoppered. When the stand was shaken, the contents of all the flasks were simultaneously mixed. The reaction was then stopped in each flask in turn by the addition of 50 ml of a 1% aqueous sodium hydroxide solution. The color of chromyl chloride was rapidly discharged.

The contents of the flasks were then analyzed for residual Cr (VI) by iodometric titration. Assuming that the precipitate contains Cr (IV), which would give, on hydrolysis, 2/3 Cr (III) + 1/3 Cr (VI), one can calculate the concentration of CrO_2Cl remaining. It was shown that this method leads correctly to $[CrO_2Cl_2]_\infty = 0$ when the hydrocarbon is in excess.

Chromyl chloride was prepared by Sisler's method (5), and probably contained some sulphate (1). Reagent grade toluene, diphenylmethane, triphenylmethane, and benzyl chloride (Eastman) were used without further purification. Reagent grade carbon tetrachloride was dried over calcium sulphate and once distilled.

The reaction curves found with toluene were not of any simple form. For example, the curve reproduced in Fig. 1, is concave downwards in the early portion. Diphenylmethane yielded apparently normal, second-order curves (Fig. 2). Triphenylmethane

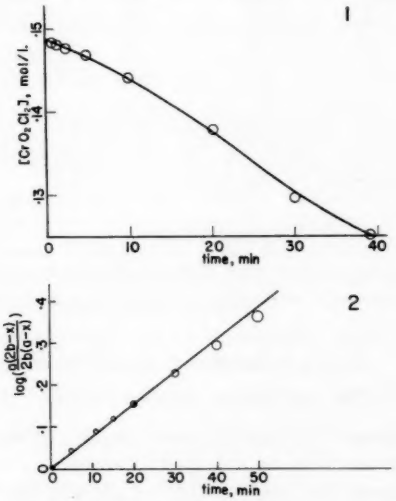


FIG. 1. Typical reaction curve with toluene (run I-A).

FIG. 2. Second-order plot for run II-D, diphenylmethane. ($\text{Log}_{10}\,[a(2b-x)]/[2b(a-x)]$ vs. time, where a and b are the initial concentrations of chromyl chloride and diphenylmethane, respectively, and x is the concentration of chromyl chloride consumed at time t.)

yielded curves that appeared normal at first but levelled out before reaching zero concentration (Fig. 3). A separate experiment showed that this was due to an oxidizing

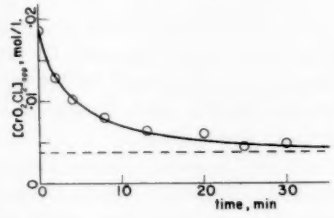


FIG. 3. Typical reaction curve with triphenylmethane (run III-B).

agent formed during the reaction, which was not extracted from the CCl_4 solution by aqueous NaOH, but which reacted slowly with aqueous KI. Such an agent could be a peroxide, resulting from air oxidation.

In view of these two complications, it was decided to base most of the conclusions on the initial rates. The partial order with respect to each reactant was determined for the three reactions by varying the initial concentrations one at a time, and noting the effect on the initial rates. The orders found are shown in Table I. They were considered close enough to unity, and the totals to two, to justify calculation of second-order rate constants. Some typical values of the rate constants are also shown in Table I, the

TABLE I

Hydrocarbon	T, °C	Order			k, l. mole^{-1} sec^{-1}	ΔH^*, kcal	p
		CrO_2Cl_2	HC	Total			
$PhCH_3$	22.1	0.94	0.98	1.92	1.28×10^{4}	14.9	10^{-4}
Ph_2CH_2	21.8	1.04	0.83	1.87	1.67×10^{-2}	12.5	10^{-2}
Ph_3CH	13.7	1.14	0.82	1.96	0.11	~3	—
$PhCH_2Cl$	30.0	—	—	(2)	1.02×10^{-4}	—	—

best known for each reaction, irrespective of temperature. For comparison, the value of k for Ph_3CH at 22° C is 0.16. That for $PhCH_2Cl$ is presumably somewhat less than 1×10^{-4}. All data are summarized in Table II.

DISCUSSION

It is clear from the reaction curves that the attack mechanism for triphenylmethane is different from that for toluene and diphenylmethane and probably involves a free radical, possibly thus:

$$(a) \quad CrO_2Cl_2 + Ph_3CH \rightarrow Ph_3C + HOCrOCl_2,$$

$$(b) \quad Ph_3C + HOCrCl_2 \rightarrow Ph_3C.O.CrCl_2OH \text{ etc.}$$

This suggestion would account for the observed oxygen absorption and would be in agreement with the known stability of the Ph_3C radical.

Ionic attack by the reagent has been postulated already by Cristol and Eilar (4) in the olefin reaction. Involvement of Cl^+ in this case is unlikely as ring attack is not observed, although it does take place in polar solvents (Carstanjen, see Hartford and

TABLE II

Summary of data

	Run	$(CrO_2Cl_2)_0$	$(HC)_0$, moles/l.	T, °C	k, l./mole-sec
Toluene	I-A	.149	.150	11.6	5.25×10^{-5}
	I-B	.149	.150	22.1	1.39×10^{-4}
	I-D	.147	.152	30.0	2.37×10^{-4}
	I-C	.148	.150	39.9	5.62×10^{-4}
	I-E	.154	.152	29.9	2.26×10^{-4}
	I-F	.309	.335	22.1	1.15×10^{-4}
	I-G	.307	.152	22.1	1.63×10^{-4}
	I-H	.311	.624	22.1	1.20×10^{-4}
	I-J	.308	1.002	22.1	1.14×10^{-4}
Diphenylmethane					
	II-B	.0495	.050	0.2	0.32×10^{-2}
	II-C	.0486	.050	21.8	1.71×10^{-2}
	II-D	.0477	.050	15.7	1.10×10^{-2}
	II-E	.0928	.115	21.8	1.55×10^{-2}
	II-F	.0928	.0573	21.8	1.74×10^{-2}
Triphenylmethane					
	III-A	.0195	.020	0.4	0.107
	III-B	.0188	.020	22.0	0.16
	III-C	.0191	.020	13.7	0.117
	III-D	.00908	.020	13.7	0.101
	III-E	.00908	.010	13.7	0.115
Benzyl chloride					
	IV-A	.1450	.159	30.0	1.02×10^{-4}

Darrin (1)). If $(CrO_2Cl)^+$ is the attacking species and if it is formed from chromyl chloride so rapidly that this ionic dissociation is not rate-determining, the kinetic data would be consistent with the following two-step process:

$$(CrO_2Cl)^+ + \text{hydrocarbon} \rightarrow \text{complex I} \qquad (k_1),$$

$$\text{complex I} + CrO_2Cl_2 \rightarrow \text{complex II} \qquad (k_2).$$

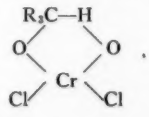
Complex I contains one chromyl chloride residue for each hydrocarbon molecule; complex II contains two for one. Such a kinetic system (6) of two consecutive, second-order steps, gives rate curves of forms dependent on the relative magnitudes of k_1 and k_2. When $k_2 \gg k_1$, the over-all reaction should approach first order with respect to chromyl chloride. This is the form of the diphenylmethane result (Fig. 2). The reaction of chromyl chloride with toluene (Fig. 1), of variable apparent order would be accommodated by having k_1 and k_2 the same order of magnitude.

The single experiment with benzyl chloride indicates a rate constant comparable with that found for toluene whereas the ionic mechanism above might be expected to predict a faster reaction. A free radical mechanism, such as that postulated for triphenylmethane, would also be expected to be faster.

Attack by the neutral chromyl chloride molecule could also fit these kinetic data. Such an attack may result in proton expulsion thus:

$$CrO_2Cl_2 + R_3CH \rightarrow (R_3C.O.CrOCl_2)^+ + H^+$$

or it may make a "four-center" activated complex of the form



which in turn could rearrange to $R_3C.O.CrCl_2OH$, or, if R_3C is a stable radical, decompose by a homolytic route. Wheeler (7) favors a π complex in solution, changing to a precipitate with two moles of chromyl chloride for each mole of hydrocarbon and with the chromium tetravalent. Both hypotheses of neutral chromyl chloride attack, as well as the $(CrO_2Cl)^+$ postulate, are in agreement with the two-step kinetic scheme advanced above.

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